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A STUDY OF THE HEATS OF DILUTION OF CERTAIN AQUEOUS SALT SOLUTIONS.

BY

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY

SUPERVISION BY ALLEN EDWIN STEARN

ENTITLED A STUDY OF THE HEATS OF DILUTION OF CERTAIN AQUEOUS SALT SOLUTIONS.

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR

THE DEGREE OF DOCTOR OF PHILOSOPHY

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I wish to express my appreciation of the suggestions of Dr. G. McP. Smith under whose supervision this investigation was carried on. To Dr. J. M. Braham I am also indebted for the use of his calorimeter and his suggestions regarding its manipulation, and to Dr. D. A. MacInnes for permission to reproduce his drawings of the apparatus. Acknowledgment is also due Mr. R. F. Schneider for assistance during the research.

Allen E. Stearn.

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INTRODUCTION

1. PURPOSE OF THE INVESTIGATION. A series of investigations (1 to 4) undertaken in this laboratory with the object of studying ionic relationships in aqueous solutions of mixed strong electrolytes has indicated the formation of higher order compounds in the ionization process, in harmony with Werner's ideas in regard to its mechanism.

The method of investigation in the papers referred to has been to study the equilibria between aqueous and metallic solutions, using mixed salt solutions and liquid amalgams. The measurement of some colligative property of aqueous solutions seemed to offer a means of testing these ideas from another point of attack, and consequently it was planned in this investigation to measure the reversible molal heats of dilution of certain mixed salt solutions and to compare these with the heats of dilution of solutions of the single salts.

2. IONIZATION OF SALTS. The simple theory of ionization as put forth by Arrhenius suggests almost directly the assumption of the isohydric principle, and this principle has been almost as fundamental as the hypothesis itself in dealing with mixed solutions. The extreme complexity of water itself would suggest at once that no such simple laws might be expected to hold quantitatively except possibly in dilute solutions, and yet superficial conductance measurements by Arrhenius (5) Barnwater (6) Sandoninni, (7) Sherril, (8) and others have indicated that

the principle is valid. Thus they found that the values obtained for the specific conductance of a mixture agreed with those calculated additively from the specific conductivities of the separate salts at equivalent concentrations. These calculations are based on the assumption that the ion fractions are directly proportional to the mol fraction of the salts. It has been shown in the series of researches already referred to on the distribution equilibrium of various pairs of molecular species between two nonmiscible phases that this assumption is actually not true. For instance it has been shown that "inequivalent mixtures of potassium and strontium chlorides, the simple strontium-ion fraction decreases while the simple potassium-ion fraction correspondingly increases with increasing total salt concentration."(4) In the same way, in the case of mixed sodium and strontium chloride solutions(3) the sodium-ion fraction gained on the strontium-ion fraction: and even in the case of such similar salts as sodium and potassium chlorides the sodium-ion fraction gained, though not so much, on the potassium-ion fraction.(2)

It is common knowledge that the various methods of measuring degree of ionization give varying results. Indeed it seems that even the approximate agreement of the conductivity method, the results of which are arbitrarily taken as representing the truth, with the values obtained from colligative property methods is due to a chance compensation of opposite influences in the latter method. Washburn(9) suggests that, although in dilute aqueous solutions the activity of an ion species is roughly proportional to its concentration, yet as a matter of fact the ion fugacity, as

he suggests, has been found to decrease with increasing concentration of the ion species. On the other hand, the fugacity of a molecular species increases very greatly with increase in concentration. In dilute aqueous solutions of strong electrolytes we have, in general, a large number of ions present and a comparatively small number of undissociated molecules; hence when we measure a colligative property of a solution which is a measure of the various activities or fugacities of the different ion or molecular species in the solution, we happen to get nearer a measure of their various concentrations than though the two types of species, ion and molecular, should act more nearly alike.

3. HEATS OF DILUTION. The reversible molal heat of dilution, L_D, of an aqueous solution at any concentration is represented by the difference in the heats of vaporization of one mol of water from a solution of that concentration and from pure water.

Thus: $L_D = \overline{L}_V - L_V$

Here L_D IS THE REVERSIBLe molal heat of dilution, $\overline{L}_V$ is the heat of vaporization of one mol of water from the solution in question, and L_V is the heat of vaporization of one mol of water from pure water.

But $\frac{d(\ln P)}{dT} = \frac{L}{RT^2}$ or $L = RT^2 \frac{d(\ln P)}{dT}$ (Clausius-Clapeyron)

Thus

$$L_D = RT^2 \frac{d(\ln P/P_o}{dT} \qquad (10)$$

Without a large mass of experimental data on the partial vapor pressure of water in solutions of various concentrations and

and at various temperatures there is no method of calculating the value of L_D without assuming Raoult's law for cases where we know it does not hold. For dilute solutions where Raoult's law does hold the ratio P/P_0 approaches unity so that L_D is zero. In concentrated solutions, however, "or in dilute solutions where the process of dilution is associated with the formation of new molecular complexes, or with the decomposition of those already occurring, the heat of dilution may have a positive or negative value."(11)

If, now, one should measure the reversible molal heat of dilution for a given concentration of solutions of single salts, and then for an equivalent concentration of a solution of the mixed salts, one might expect to find the value in the latter case to be somewhere near the sum of the other values unless affected by the formation of new molecular complexes.

MATERIALS.

The strontium chloride was in the form of Merk's "pure crystals". Most of the material was recrystallized once from water. This proceedure in the light of our results seems unnecessary, when it is considered that the heat effects in solutions as concentrated as 0.2 normal were so small as to be hardly measurable. The sodium and potassium chlorides were of various brands, all labeled C. P. These materials are easy to obtain in a state of high purity, and inasmuch as small amounts of impurities have no effect on the results in this work, it was considered unnecessary to purify them further.

APPARATUS.

THE CALORIMETER used was a very slight modification of the adiabatic calorimeter of MacInnes and Braham.(12) The calorimeter proper is outlined in cross section in Fig. 2 and a view from the top is shown in Fig. 1. These figures, together with Figs. 3, 4 and 5, are taken by kind permission of Dr. MacInnes from MacInnes' and Braham's article on the instrument. The calorimeter vessel A-A, a ten liter vessel made of heavy copper and nickle plated, is separated from a similar surrounding vessel B-B by a 6mm. air space. The separation is effected by a rubber gasket a, and a supporting ring of hard rubber, o. The seams of both vessels are brazed. B-B is supported on brass legs, b, that fit into holes in a wooden false bottom in a larger vessel, C. "The vessel B-B carries the cover M-M of 3mm. brass which can be clamped on the 2cm. flange of B-B. A rubber gasket, e-e, is in-

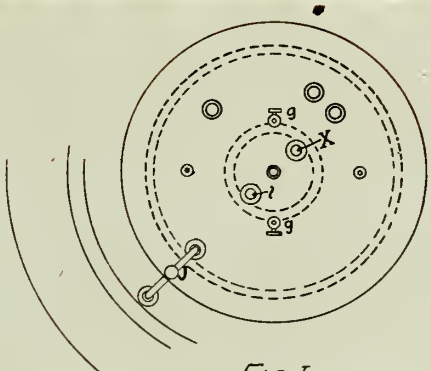
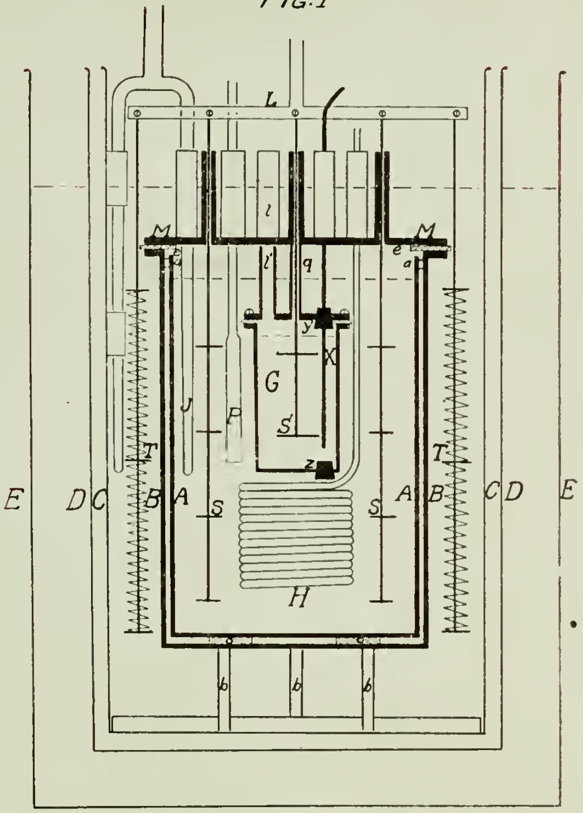


FIG. I


L
l
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D
C
B
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S
A
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C
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E
H
b
b
b

FIG. 2

terposed between the cover and the flange. Screwed into the cover are a number of tubes, each two inches long, through which pass the platinum resistance thermometer, P, the leads from the heater, H, the arms from the stirrers, S-S, and S', the wire supports,g-g, of the dilution cup, G, one leg of the thermojunction, J, and the rod, X. The tube, l, is for the purpose of filling the dilution cup.

"The sides of the dilution cup, G, are made of thin sheet copper fastened to a brass ring at the top and to a sheet brass bottom. A brass cover 3mm. thick carries the tubes l' and q. This cover makes a water-tight connection with the ring at the top of the cup by means of the rubber gasket and screws as shown. The tube l' fits under l, and is used for filling the cup. The stirrer S' passes through the tube q. In a vertical line under a tube in the calorimeter cover M-M two holes, y and z, are bored in the cover and bottom of the dilution cup. The hole y is closed by a rubber stopper fastened to a brass rod, X; the holes y and z can be opened in turn. The cup is held in place by means of wires fastened into tubes in the cover M-M."

The stirrer S-S consists of four brass disks with holes punched in them at intervals.

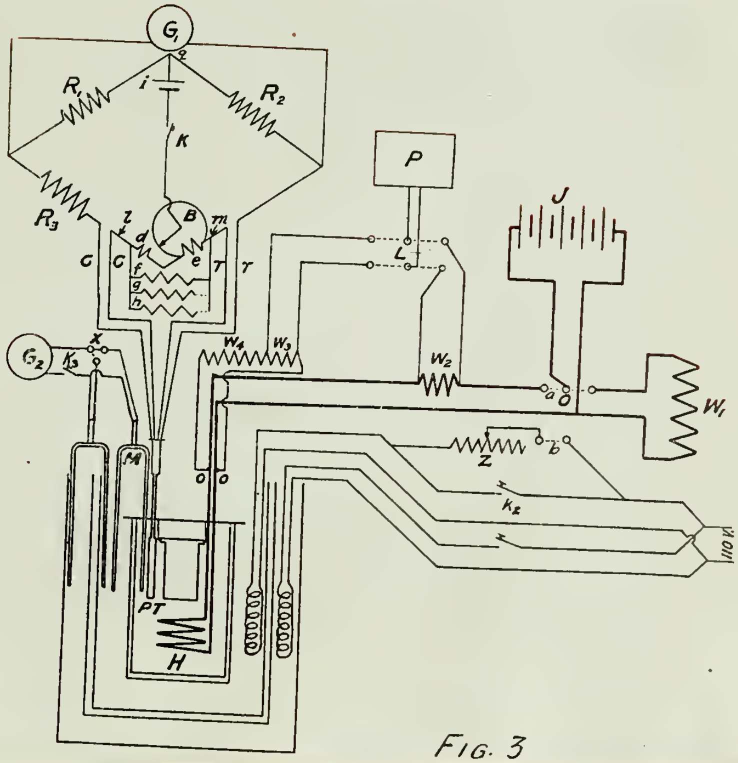
The space between the vessels B and C is filled with water. This space will be referred to as the "surroundings". In this space is placed a stirrer T-T, consisting of three galvanized iron disks each containing eight holes. "This stirrer carries four coils each containing eight meters of number 18 nichrome wire. The coils pass through the stirrer disks on wooden insula-

tors and are arranged diagonally to the direction of motion of the stirrer. These coils are connected in series through a key to a source of 110 volt alternating current. "Thus the temperature of the surroundings can be raised at any time.

"The stirrers S-S, S', and T-T are all connected to the yoke L, which is given an up and down motion of 5cm. sixty times a minute by means of a crank operated through a system of pulleys by a one sixth horse power motor. This method of stirring has been demonstrated to be extremely efficient.

"The vessels C, D, and E are of heavy galvanized iron. Vessel D is separated from vessel C by an air space." The space between vessels D and E is filled with water. This in itself gives a rough regulation of the radiation from the "surroundings". This regulation may be made easier by regulating the temperature of the water in this space by means of a stirrer and heating coils much the same as the system in the space between vessels B and C.

THE PLATINUM RESISTANCE THERMOMETER was one designed by Dickinson and Mueller (13) and made by Leeds and Northrup. The resistance of the thermometer was measured by means of a Wheatstone bridge designed also by Dickinson and Mueller and manufactured by Leeds and Northrup. The upper right hand corner of Fig. 3 shows a diagram of the bridge and connections. R_3 is an adjustable resistance of 100 ohms, the lowest coils being 0.01 ohm. In this arm of the bridge the compensative leads, c-c, of the thermometer are placed in series. The main leads, T-T, of the thermometer are connected in the remaining arm. R_1 and R_2 repre-



G₁
R₁
i
R₂
K
R₃
B
l
m
d
e
c
C
T
T
f
g
h
P
L
J
W₄
W₃
W₂
W₁
G₂
X
K₃
M
a
O
o
o
Z
b
K₂
PT
H
110 V.

FIG. 3

sent the ratio coils. Those used were 100 ohms each. The bridge wire, B, shunted by a resistance, e, is also placed in the arm with the main thermometer leads. " 'd' is a resistance equal to that of the shunted bridge wire, 0.55 ohms. The shunts f, g, and h are so arranged that the resistance between the points l and m can be adjusted to 0.11, 0.22, or 0.55 ohm, equal respectively to the increase in resistance when the temperature of a 25 ohm thermometer is increased roughly 1.1°, 2.2°, or 5.5°. The shunt which gives a change in resistance corresponding to 1.1° is the one which was used. Since each turn of the bridge wire is graduated in 200 divisions which can be readily estimated to fifths, temperature changes corresponding to 0.0001° can be read with ease.

"A dry cell, i, is connected through a key, k, between the junction of the ratio coils, q, and the sliding contact on the bridge wire, d."

The galvanometer, G, is a Leeds and Northrup "high sensitivity" galvanometer with a sensitivity of about 2mm. per microvolt at a scale distance of one meter. Its resistance is 13.5 ohms.

"A DIFFERENTIAL THERMOMETER, M (Fig. 3), consisting of a set of sixteen copper-constantin thermojunctions is employed to measure the constant temperature difference maintained between the calorimeter and 'surroundings' during a determination." The instrument is connected in series with a galvanometer in such a way that a temperature difference of 0.15° gives a deflection of about 20mm. at a scale distance of one meter. It is connected

through a key, k_3, so that the circuit may be opened at any time and any shift from the zero position corrected. During a part of this work another set of thermojunctions, less sensitive, was placed between the "surroundings" and the outer bath. By means of a double switch, X, the same galvanometer, G_2, can be used with either set of junctions.

THE HEATERS AND CONNECTIONS are shown on the right side of Fig. 3. The source of heat for the calorimeter coil, J, consisted of a storage battery arranged to deliver 10 volts. By means of the switch at 'o' the current can be made to pass through the heater H, or through a polarizing resistance W_1, equal to the resistance of the heater. A preliminary polarization of the cells by passing the current through W_1 insures a steadier current when they are connected to the heater.

W_2 is an accurately known resistance of 0.6419 ohm in series with the heater. It is designed to carry up to three amperes without changing its resistance. From the terminals of W_2 leads are run to the double throw switch L, and thence to the potentiometer, P. From the potentiometer reading and the value of W_2 the current passing through the heater can be calculated.

"The resistances W_3 and W_4 are shunted across the terminals O-O of the heater H. W_4 is 10,000 ohms and W_3 is adjusted so that the voltage at its terminals is approximately equal to the potential drop through W_2." The potential drop across W_3 can also be read on the potentiometer P by adjustment of the switch L. From this value and a knowledge of the values of W_3 and W_4 the E. M. F. drop through the heater can be obtained. The potentiometer

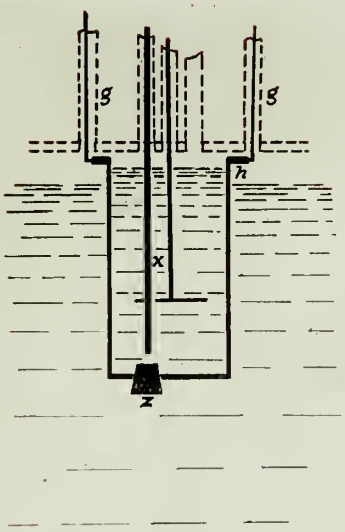


FIG. 4

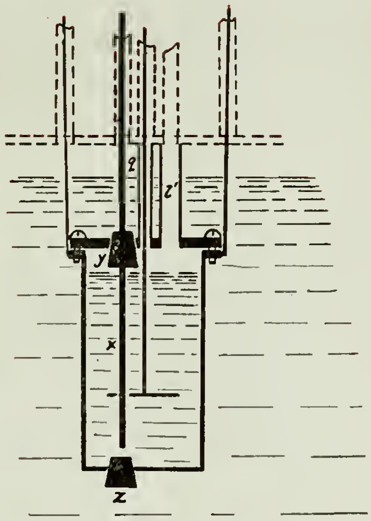


FIG. 5

is equipped with a Leeds and Northrup portable galvanometer of one megohm sensitivity. It is adjusted by means of a Weston standard cell. The time during which current is passed into the heater is measured by means of a stop watch which has been repeatedly compared with an accurate clock.

The simultaneous introduction of heat into the calorimeter and "surroundings" is brought about by the switch at 'o'. The connectors 'a' and 'b' work together so that when the current from the storage battery is shifted from the polarizing resistance to the heater, the alternating current from a 110 volt source is at the same time sent through the coils in the "surroundings". The rheostat, z, is in series with the alternating current, and the sliding contact is so placed as to keep the difference in temperature between the calorimeter and the "surroundings" constant, leaving the operator free to read the potentiometer. A key, k_2, is arranged so as to be able to "short" the full strength of the alternating current through the coils of the "surroundings". The external bath is provided with a similar arrangement not shown in the diagram.

Fig. 5 shows the design of the dilution cup. With this design, which is an improvement over that shown in Fig. 4 - one of the previous designs - the "dilution of water with water is unaccompanied by any heat effect." Holes y and z, in a vertical line under a tube in the calorimeter cover, are closed with rubber stoppers, one of which is attached to the rod, X. "The entire cup is submerged in the liquid in the calorimeter. To operate, the rod X is pushed down, carrying the stopper in the hole

'y' with it. The solution rushes into the free space in the cup. The stopper in 'z' is then displaced and the circulation through the cup soon causes thorough mixing."

In making a calorimetric determination, a weighed quantity of a salt solution of a known concentration is introduced into the calorimeter vessel. The apparatus is then assembled and a weighed amount of water introduced through tubes 1 and 1' (Fig. 2) into the dilution cup. The "surroundings" are filled with water at a temperature slightly lower than that of the solution in the calorimeter. The differential thermometer and the platinum resistance thermometer are inserted and stirring commenced. The "surroundings" are then slowly heated by closing key k2 intermittently until the difference in temperature between them and the calorimeter liquid is about 0.15° as shown by the throw of galvanometer G_2. After one to three hours, giving time for complete uniformity of temperature in the dilution water and the solution, readings of the temperature of the calorimeter are taken until they are constant to 0.0001° for from five to ten minutes.

From here on the proceedure varies according to whether the heat of dilution, as determined by a preliminary trial, is positive or negative. If it is positive, the solution is directly diluted, and after allowing sufficient time for mixing, constant temperature readings are again obtained. Next, current is passed through the heater for a known length of time, and finally the temperature is again read when constant. The proceedure in the case of negative heats where these are comparitively large,

is to introduce heat into the solution by means of the electric current at a slightly more rapid rate than it is taken up in dilution. Then, after finishing the run as described above, one can calculate the number of calories corresponding to the electrical energy introduced, and the actual number of calories corresponding to the increase in temperature. The difference would be the number of calories due to the heat of dilution. By this proceedure the heat capacity of the calorimeter is measured as a part of every determination, and thus inaccuracies due to calculations from questionable data on specific heats of solutions, water equivalent of the calorimeter, slightly varying conditions of experiments, uncertainties arising from the calibration of the thermometer, etc. are eliminated. Thus by a simple proportion the heat of dilution can be obtained at once. For if H_D is the heat due to dilution, expressed in joules, then

$$H_D : EIT = R_D : R_E$$

where E is electromotive force, I the current, and T the time in seconds during which the current is passed through the calorimeter. R_D and R_E are the changes in temperature, in resistance units, due respectively to the dilution and to the electrical heating.

$$\text{or} - H_D \text{ (in calories)} : \frac{EIT}{J} = R_D : R_E$$

where J represents Joule's equivalent, 4.184 joules per calorie.

Since the relation between the change in resistance and the temperature change is not linear, any large values of R_D or R_E would have to be corrected by means of the relation,

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Since the relation between the change in resistance and the temperature change is not linear, any large values of R_D or R_E would have to be corrected by means of the relation,

$$\Delta t = \frac{100}{(R_{100} - R_0)\left(1 + \frac{d'}{100} - \frac{2d'T}{100^2}\right)} \Delta R,$$

in which R_{100} is the resistance of the thermometer in steam at 760 mm. Hg. pressure, R_0 is its resistance in melting ice, and d' is an empirical constant. MacInnes and Braham determined R_{100} and R_0 for the thermometers employed, and used for d' the value 1.47, recommended by the Bureau of Standards. They found, however, that with the values of R_D, and R_E of the magnitude met with in their work, which were even greater than those met with in this investigation, the correction was too small to affect their numerical results in any way; so that if $\Delta R = 0.0239\underline{5}$, then $\Delta t = 0.239\underline{5}$, just ten times the numerical value of ΔR.

METHOD.

The salt solutions were made up on the basis of gram equivalents of anhydrous salt per one thousand grams of water. Their concentration was determined by a Volhard determination of the chlorine. The salts used were sodium chloride, potassium chloride and strontium chloride; and the concentrations at which the heats of dilution were determined were 0.2 weight normal, 0.4 weight normal, 0.8 weight normal, 1.6 weight normal, and 3.2 weight normal, where, as before stated, they are expressed in gram equivalents per one thousand grams of water. Points on the strontium chloride curve were also obtained for concentrations

of 1.2, 2.0, 2.4, and 2.8 weight normal.

Mixed salt solutions of $1NaCl:1/2SrCl_2$, $1NaCl \cdot 1KCl$, $1KCl \cdot 1/2SrCl_2$, and $1KCl \cdot 1SrCl_2$ were also run at the above mentioned concentrations. These solutions were prepared by diluting a volume of the solution of one of the salts with an equal volume of the solution of the same concentration of the other salt. Thus one volume of 0.8 weight normal KCl and one volume of 0.8 weight normal NaCl were mixed and called 0.8 weight normal of the mixed salt.

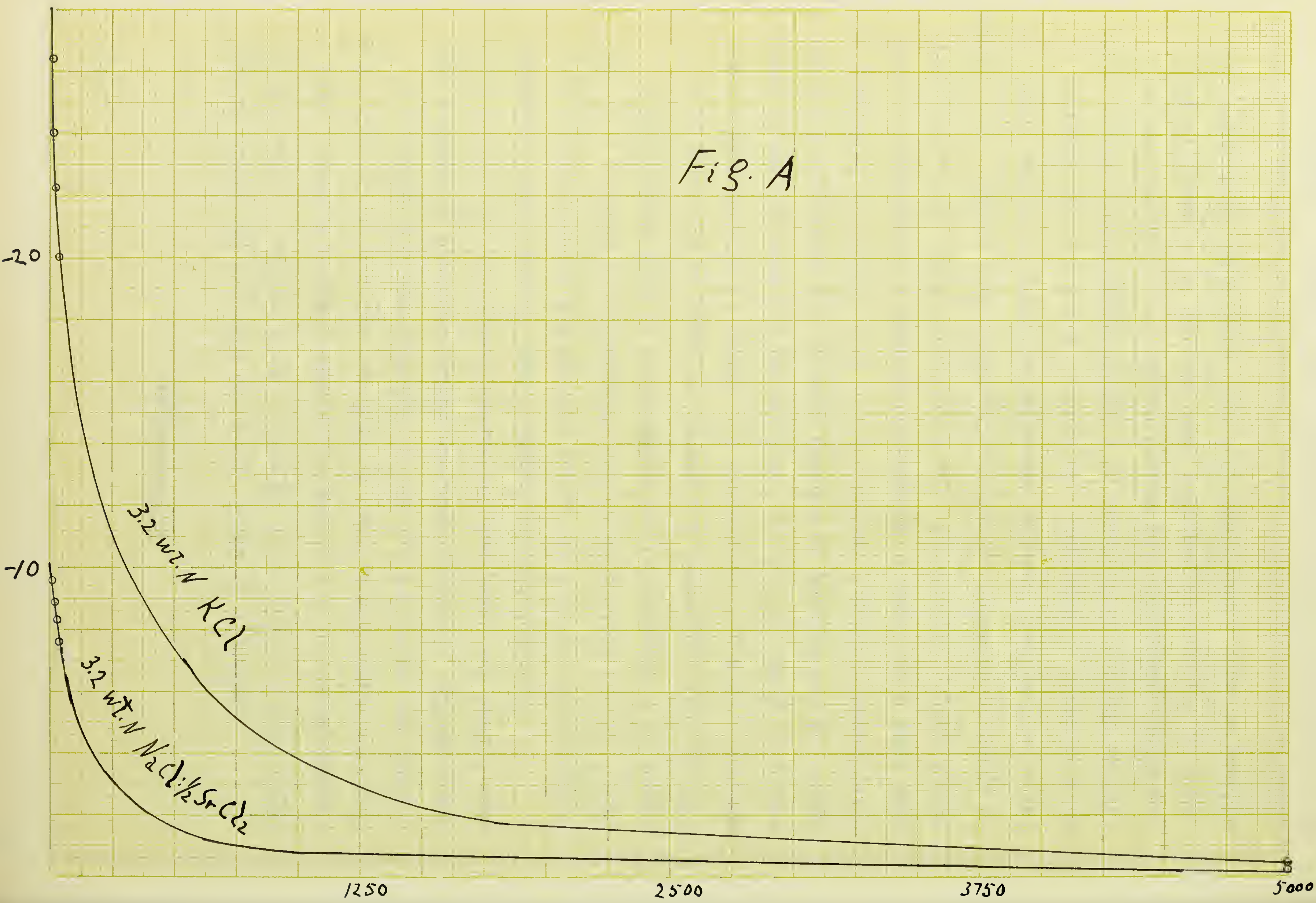
The value of the reversible molal heat of dilution was obtained by diluting the solution at a definite concentration with decreasing amounts of water, and plotting the heat effect obtained against the number of mols of water added. The curve was found to be a straight line (at this region) so that, by extrapolation to zero mols of water added ,the value of the reversible molal heat of dilution at any concentration could be obtained. That is; this value would approximate the quantity of heat absorbed or evolved when one mol of solvent is added to an infinite quantity of solution.

ACCURACY. The very small values of the heat effects in the case of the more dilute solutions necessitated only approximate results here. MacInnes and Braham state that heat effects of from 50 to 60 calories can be measured with an accuracy of from four to five per cent. With a total heat effect of from 5 to 20 calories one should not expect much more than 30 to 50 per cent accuracy. In these cases, however, an error of even 100 per cent would change the point on the curve of the concen-

tration plotted against the molal heat effect to such a slight extent that the curve itself would be unaffected. In the case of the larger heat effects, running as high as 600 to 700 calories, the heat changes can be measured to within one fourth to one half of one per cent, so that the error of the reversible heat value should not be greater than one to two per cent.

Some justification for the assumption that the molal heat values obtained by diluting a certain quantity of solution with varying amounts of water give a straight line when plotted against the number of mols of water of dilution is given in Figure A. The data for these curves is taken from Tables VI, XXV, and XL on pages 24, 44, and 61 respectively. According to Thomsen (20) "the value of the thermal change on dilution always varies with variations in the quantity of water of dilution, and this variation, whether positive or negative, seems to have the character of a hyperbolic function of the quantity of water added." As will be seen, the region of the curve on which the experimental data represented in all of the remainder of the curves is taken is far enough from the vertex that the change of slope of the curve has become vanishingly small, and it is practically a straight line. (In Figure A, mols of water of dilution per 10,000 grams of solution are plotted as abscissae, and the molal heat effects as ordinates.)

Fig. A



EXPERIMENTAL.

Tables I to XXXIX give the data for the heats of dilution of the various salt solutions and mixtures. A few curves representative of the method of extrapolation are given. Fig. 6 gives the curve for 1.6 wt. N. NaCl and for 1.6 wt. N. KCl. Fig. 7 gives the curve for 3.2 wt. N. KCl-NaCl and for 3.2 wt. N. KCl-1/2$SrCl_2$. In most cases the values obtained by drawing similar curves are given but the curves themselves are not included.

In the following tables 'Time' is the time in seconds during which the heat is passed through the calorimeter heater; 'Res.' is the resistance of the thermometer in ohms; Δ R is the change of resistance of the thermometer in ohms multiplied by 10^5;'Gm.Sol! represents the number of grams of solution to be diluted; 'Mols H_2O' represents the number of mols of water (assuming 18 grams to the mol.) with which the solution was diluted; 'Amp.' is the current in amperes through the heating coil of the calorimeter; 'E.M.F.' is the voltage drop across the terminals of this same coil; 'Cal.' represents the number of calories of electrical energy introduced. The total heat effect of the dilution is given in calories as well as the molal heat effect. The latter value is obtained from the former by dividing it by the number of mols of water of dilution. In general there are two types of tables, the one in the case of a LARGE negative heat effect where electrical energy was introduced during the dilution, and the other in the case of positive heat effects or of negative heat effects of such a magnitude that the temperature difference be-

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

tween the calorimeter and the "surroundings" could be easily regulated without this added step. In each case one sample calculation is given.

Fig. 6

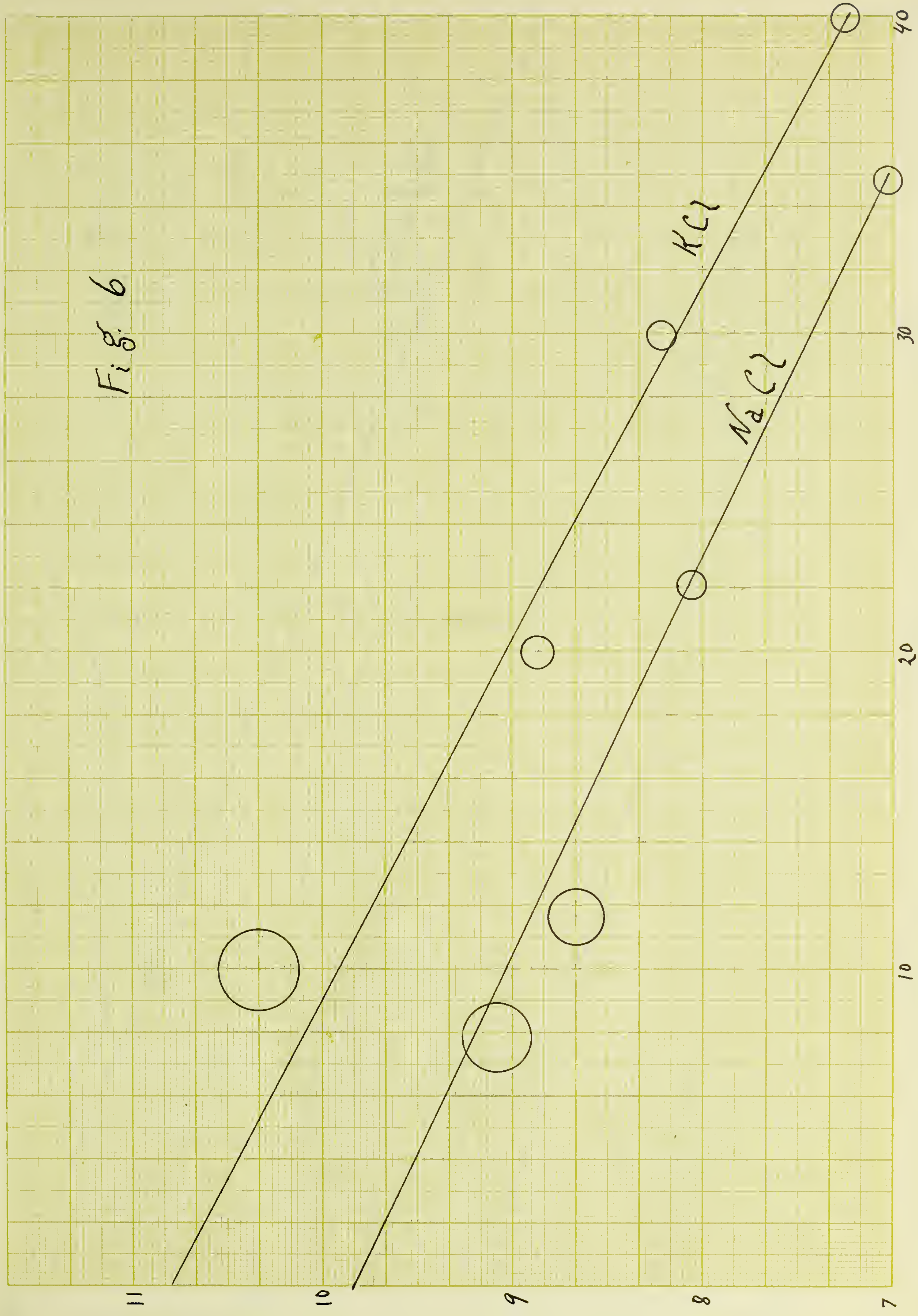


Fig. 7

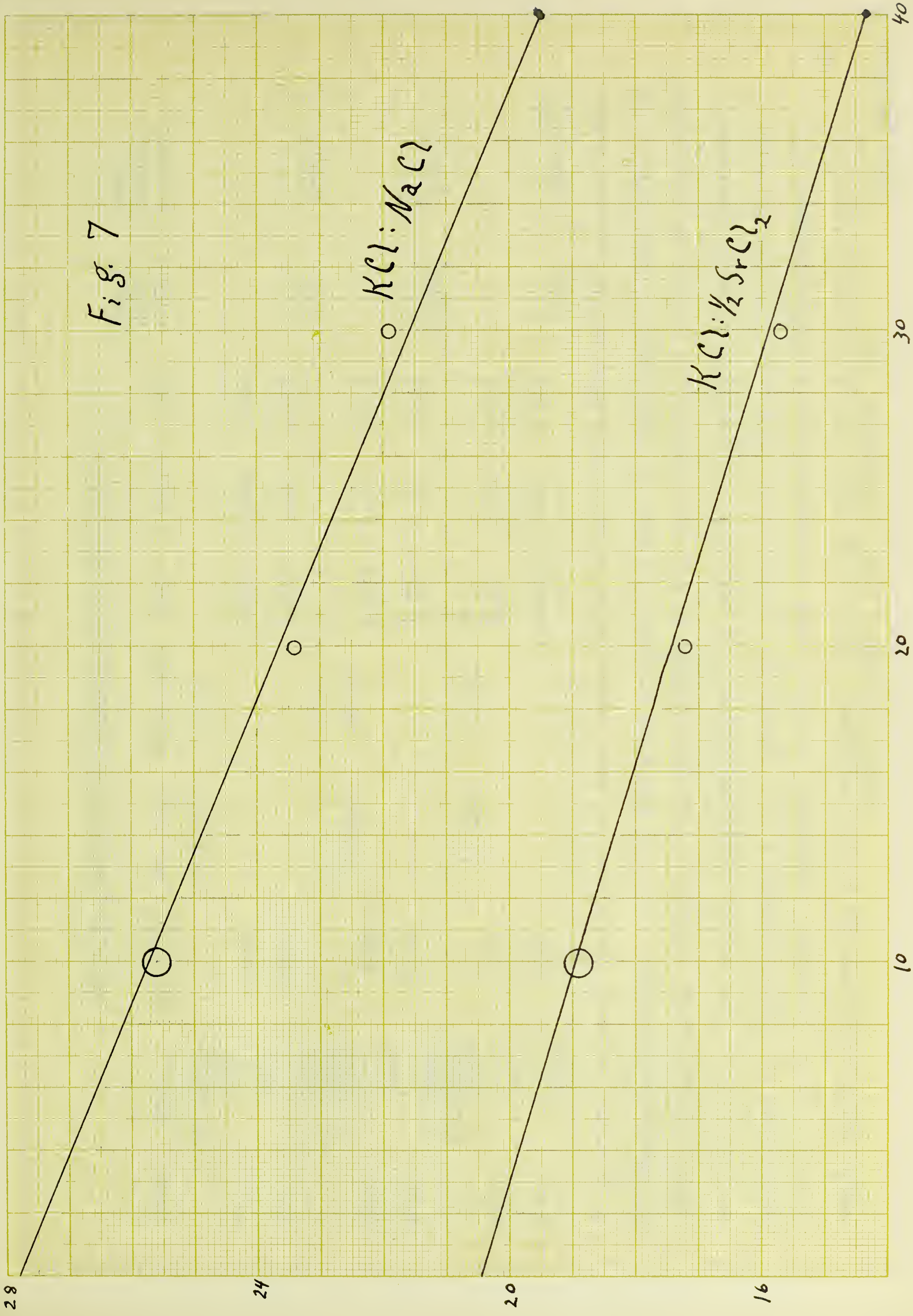


Table I - Heat of Dilution of 3.2 wt.N.* NaCl.

Time	Res.	$\Delta R \times 10^5$	Gm. Sol.	Mols H_2O.	Amp.	E.M.F.	Cal.	Total Heat Effect	Heat Effect per Mol.
	27.41500		10,586	27.4					
	3205								
300		670			2.322	6.635	1105		
	3875								
303		1315			2.305	6.58	1099		
	5190							-546	-19.9
	27.43500								
	2795		10,586	18.45					
300		810			2.335	6.66	1115		
	3605								
300		1260			2.334	6.66	1115		
	4865							-398	-21.6
	27.45500								
	2862		10,586	11.22					
300		946			2.33	6.65	1111		
	3808								
300		1235			2.335	6.66	1115		
	5043							-258	-22.95**

* By wt.N. is meant the number of gram equivalents of anhydrous salt per 1000 grams water.

** Sample Calculation. If 1099 calories produce a change in resistance of 1315 units, then 1105 calories would produce in the same amount of the same solution a change of resistance of 1323 units. The change measured however was only 670. A quantity of heat therefore equivalent to that represented by a change of resistance of 1323 minus 670 or 653 units was used up by dilution. Therefore if 1315 units are equivalent to 1099 calories, 653 units would be equivalent to 546 calories. This value, then, would represent the heat

REVERSIBLE MOLAL HEAT OF DILUTION, L_D, -25. cal/mol

Table II - Heat of Dilution of 1.6 wt.N. NaCl.

Time	Res.	$\Delta R \times 10^5$	Gm. Sol.	Mols H_2O	Amp.	E.M.F.	Cal.	Total Ht. Effect.	Heat Effect per Mol.
	27.47500								
	2934		8,280	34.83					
200		560			2.33	6.65	740.7		
	3494								
300		1255			2.33	6.65	1111		
	4749							-245.	-7.04
	27.49500								
	2792		8,280	22.06					
200		594			2.305	6.57	724.		
	3386								
300		1206			2.32	6.62	1101.		
	4592							-179.	-8.06
	27.51500								
	2029		8,280	11.75					
200		661			2.317	6.60	731		
	2690								
300		1170			2.335	6.65	1113.4		
	3860							-102.	-8.67
	27.53500								
	1604		8,280	7.83					
200		700			2.335	6.66	743.4		
	2304								
300		1160			2.335	6.66	1115.		
	3464							-71.1	-9.08

Reversible Molal Heat of Dilution, L_D, - - - - - -9.8 cal./Mol.

(**) effect due to dilution with 27.4 mols of water. The molal heat effect would then be 546 divided by 27.4 or 19.9 calories. The sign would of course be negative.

Table III - Heat of Dilution of 0.8 wt.N. NaCl.

Time	Res.	$\Delta R \times 10^5$	Gm. Sol.	Mols H_2O	Amp.	E.M.F.	Cal.	Total Ht. Effect.	Heat Effect per mol.
	27.59500								
	3169		7,986	36.45					
100		328			2.33	6.66	371.		
	3497								
300		1210			2.33	6.66	1112.6		
	4707							-70.	-1.92
	27.61500								
	1693		7,986	32.86					
200		653			2.335	6.68	745.6		
	2346								
300		1090			2.335	6.66	1115.		
	3436							-77.8	-2.37
	27.59500								
	3519		7,986	25.65					
100		325			2.345	6.675	374		
	3844								
300		1195			2.335	6.655	1114.2		
	5039							-70.9	-2.76
	27.61500								
	1745		7,986	16.75					
100		334			2.334	6.65	371.3		
	2079								
300		1150			2.335	6.65	1114.		
	3229							-48.44	-2.89

REVERSIBLE MOLAL HEAT OF DILUTION, L_D, -3.93 Cal./Mol.

Table IV - Heat of Dilution of 0.4 wt.N. NaCl.

Time	Res.	$\Delta R \times 10^5$	Gm. Sol.	Mols H_2O	Amp.	E.M.F.	Cal.	Total Ht. Effect.	Heat Effect per Mol.
	27.35500								
	2733		7,900	37.72					
		-33							
	2700								
300		1230			2.323	6.633	1104		
	3930							-29.62	-0.79**
	27.36500								
	2305		7,900	25.58					
		-25							
	2280								
300		1150			2.335	6.619	1108		
	3430							-24.09	-0.94
	27.36500								
	2397		7,900	21.5					
		-28							
	2369								
300		1210			2.3155	6.605	1097		
	3579							-25.38	-1.18
	27.36500								
	2900		7,900	16.5					
		-22							
	2878								
300		1150			2.326	6.518	1105.5	-21.15	-1.28

Table IV.(Cont'd) Heat of Dilution of 0.4 wt.N. NaCl.

Time	Res.	$\Delta R \times 10^5$	Gm. Sol.	Mols H_2O	Amp.	E.M.F.	Cal.	Total Ht. Effect	Heat Effect per Mol.
	27.36500								
	2503		7,900	12.47					
		-18							
	2485								
100		385			2.321	6.6189	367		
	2870							-17.16	-1.38
	27.36500								
	2128		7,900	8.86					
		-13							
	2115								
200		764			2.3215	6.6185	734.5		
	2879							-12.48	-1.41

REVERSIBLE MOLAL HEAT OF DILUTION, L_D, -1.6 Cal/Mol.

** Sample calculation. (See page 21 for data) If a resistance change of 1230 units corresponds to 1104 calories, then a change of 33 units would correspond to 29.62 calories. This is the heat effect for 37.72 mols of water. The molal heat effect, then, would be 29.62 divided by 37.72 or 0.79 calories. In this case the effect is negative since the resistance DECREASED by 33 units on dilution. The calculation is the same in the case of positive heats, however, except for the change of sign.

Table V - Heat of Dilution of 0.2 wt.N. NaCl.

Time	Res.	$\Delta R \times 10^5$	Gm. Sol.	Mols H_2O	Amp.	E.M.F.	Cal.	Total Ht. Effect	Heat Effect per Mol.
	27.33500								
	2140		9,300	28.8					
		-17							
100	2123								
		210			1.788	5.098	218		
	2333							-17.64	-0.61
	27.29500								
	2195		9,300	23.4					
		-20							
	2175								
200		470			1.755	5.013	421		
	2645							-17.9	-0.765
	27.24500								
	2404		9,300	18.11					
		-15							
	2389								
200		480			1.773	5.053	428		
	2869							-13.4	-0.74
	27.24500								
	2533		9,300	14.6					
		-11							
	2522								
200		470			1.771	5.049	427.4		
	2992							-10.	-0.69

REVERSIBLE MOLAL HEAT OF DILUTION, L_D, -0.85 cal/mol

Table VI - Heat of Dilution of 3.16 wt.N. KCl.

Time	Res.	$\Delta R \times 10^5$	Gm. Sol.	Mols H_2O	Amp.	E.M.F.	Cal.	Heat Effect.	Heat Effect per Mol.
	27.25500								
	0618		8,410	39.					
500		367			1.77	5.050	1068		
	0985								
500		1370			1.772	5.0533	1070		
	2355							-781.	-20.03
	27.19500								
	2355		8,410	26.55					
500		560			1.77	5.05	1068		
	2915								
500		1300			1.7775	5.067	1076		
	4215							-604.3	-22.76
	27.16500								
	1152		8,410	19.4					
500		702			1.79	5.10	1091		
	1854								
500		1263			1.788	5.094	1089		
	3117							-484.	-24.94
	27.15500								
	0987		8,410	14.4					
500		777			1.79	5.05	1080		
	1764								
500		1200			1.778	5.068	1077		
	2964							-382.2	-26.48
	27.14500								
	0454		8,410	9.4					
500		923			1.80	5.152	1108		
	1377								
500		1190			1.79	5.0997	1091		
	2567							-261.2	-27.79

REVERSIBLE MOLAL HEAT OF DILUTION, L_D, -30. cal/mol.

Table VII - Heat of Dilution of 1.6 wt.N. KCl.

Time	Res.	$\Delta R \times 10^5$	Gm. Sol.	Mols H_2O	Amp.	E.M.F.	Cal	Total Ht. Effect.	Heat Effect per Mol.
	27.34500								
	2120		8,000	40.					
500		885			1.762	5.004	1054		
	3005								
500		1200			1.743	4.978	1037		
	4205							-289.5	-7.24
	27.34500								
	1522		8,000	30.					
500		892			1.751	5.004	1047		
	2414								
500		1160			1.748	4.982	1041		
	3574							-246.7	-8.22
	27.29500								
	3659		8,000	20.					
		-185							
	3474								
500		1086			1.748	4.982	1041		
	4560							-177.2	-8.87
	27.30500								
	2900		8,000	10					
		-101							
	2799								
500		980			1.729	4.852	1003		
	3779							-103.3	-10.33

REVERSIBLE MOLAL HEAT OF DILUTION, L_D, -10.8 cal/mol.

Table VIII - Heat of Dilution of 0.8 wt.N. KCl.

Time	Res.	$\Delta R \times 10^5$	Gm. Sol.	Mols H_2O	Amp.	E.M.F.	Cal.	Total Ht. Effect.	Heat Effect per Mol.
	27.34500								
	2821		8,000	40.					
		-80							
	2741								
300		2060			2.983	8.51	1820		
	4801							-70.68	-1.77
	27.34500								
	3240		8,000	30					
		-70							
	3170								
200		1400			3.084	8.805	1298		
	4570							-64.9	-2.16
	27.37500								
	3108		8,000	20					
		-50							
	3058								
200		1300			3.048	8.702	1268		
	4358							-48.8	-2.44
	27.37500								
	3581		8,000	10					
		-28							
	3553								
200		1280			3.053	8.702	1270	-27.8	-2.78
	4833								

REVERSIBLE MOLAL HEAT OF DILUTION, L_D, -3.2 cal/mol.

Table IX - Heat of Dilution of 0.4 wt.N. KCl.

Time	Res.	$\Delta R \times 10^5$	Gm. Sol.	Mols H_2O	Amp.	E.M.F.	Cal.	Total Ht. Effect	Heat Effect per Mol.
	27.29500								
	2229		8,000	34.95					
		-15							
	2214								
100		375			2.349	6.7035	376		
	2585							-15.	-0.43
	27.30500								
	3494		8,000	30.					
		-14							
	3480								
100		392			2.349	6.695	376	-13.42	-0.45
	3872								
	27.30500								
	2745		8,000	25					
		-14							
	2731								
100		375			2.354	6.708	377.5		
	3106							-14.1	-0.564
	27.30500								
	1722		8,000	20					
		-12							
	1710								
100		365			2.357	6.717	378.3		
	2075							-12.44	-0.622
	27.29500								
	2052		8,000	15					
		-9							
	2043								
100		340			2.354	6.715	378.		
	2383							-10.	-0.67

REVERSIBLE MOLAL HEAT OF DILUTION, L_D, -0.95 cal/mol.

Table X - Heat of Dilution of 0.2 wt.N. KCl.

Time	Res.	$\Delta R \times 10^5$	Gm. Sol.	Mols H_2O	Amp.	E.M.F.	Cal.	Total Ht. Effect	Heat Effect per Mol.
	27.35500								
	3165		7,850	40					
		-3							
	3162								
100		410			2.345	6.69	375		
	3572							-2.74	-0.069
	27.33500								
	2446		7,850	38.2					
		-3							
	2443								
100		392			2.364	6.735	380		
	2835							-2.92	-0.076
	27.33500								
	2520		7,850	34					
		-3							
	2517								
100		357			2.36	6.74	380		
	2874							-3.2	-0.094
	27.34500								
	1966		7,850	30					
		-3							
	1963								
100		365			2.35	6.70	377		
	2328							-3.1	-0.103
	27.35500								
	1643		7,850	30					
		-3							
	1640							-3.25	-0.108

REVERSIBLE MOLAL HEAT OF DILUTION, L_D, -0.24 cal/mol.

Table XI - Heat of Dilution of 3.2 wt.N. $SrCl_2$.

Time	Res.	$\Delta R \times 10^5$	Gm. Sol.	Mols H_2O	Amp.	E.M.F.	Cal.	Total Ht. Effect.	Heat Effect per Mol.
	27.21500								
	2577		10,000	35					
		210							
	2787								
300		1063			2.16	6.18	958		
	3840							189	5.4
	27.10500								
	2335		10,000	15					
		97							
	2432								
200		648			2.163	6.18	639		
	3080							95.7	6.4

REVERSIBLE MOLAL HEAT OF DILUTION, L_D, 7.2 cal/mol.

Table XII - Heat of Dilution of 2.9 wt.N. $SrCl_2$.

Time	Res.	$\Delta R \times 10^5$	Gm. Sol.	Mols H_2O	Amp.	E.M.F.	Cal.	Total Ht. Effect.	Heat Effect per Mol.
	27.34500								
	2042		9,500	37.2					
		135							
	2177								
300		1170			2.346	6.69	1125		
	3347							129.8	3.49
	27.37500								
	1802		9,500	30.					
		128							
	1913								
300		1280			2.343	6.69	1124		
	3210							112.4	3.75
	27.33500								
	2920		9,500	30.					
		125							
	3045								
300		1240			2.352	6.708	1131		
	4285							114.1	3.8
	27.29500								
	1935		9,500	27.7					
		125							
	2060								
500		1250			1.791	5.103	1092		
	3310							109.2	3.95

Table XII (Cont'd) - Heat of Dilution of 2.9 wt.N. $SrCl_2$.

Time	Res.	$\Delta R \times 10^5$	Gm. Sol.	Mols H_2O	Amp.	E.M.F.	Cal.	Total Ht. Effect.	Heat Effect per Mol.
	27.34500								
	2210		9,500	20					
		90							
	2300								
300		1170			2.343	6.681	1122		
	3470							86.33	4.31
	27.25500								
	3143		9,500	19.5					
		92							
	3235								
500		1170			1.7865	5.089	1087		
	4405							85.44	4.38
	27.31500								
	1962		9,500	10					
		48							
	2010								
200		745			2.349	6.704	753		
	2755							48.5	4.85

REVERSIBLE MOLAL HEAT OF DILUTION, L_D, 5.4 cal/mol.

Table XIII - Heat of Dilution of 2.4 wt.N. $SrCl_2$.

Time	Res.	$\Delta R \times 10^5$	Gm. Sol.	Mols H_2O	Amp.	E.M.F.	Cal.	Total Ht. Effect.	Heat Effect per Mol.
	27.23500								
	1990		10,000	35					
		40							
	2030								
200		775			2.18	6.26	653		
	2805							33.7	0.96
	27.18500								
	2504		10,000	25					
		35							
	2539								
200		685			2.15	6.145	631		
	3225							32.3	1.29

REVERSIBLE MOLAL HEAT OF DILUTION, L_D, 2.1 cal/mol.

Table XIV - Heat of Dilution of 2.0 wt.N. $SrCl_2$.

Time	Res.	$\Delta R \times 10^5$	Gm. Sol.	Mols H_2O	Amp.	E.M.F.	Cal.	Total Ht. Effect.	Heat Effect per Mol.
	27.33500								
	2420		10,000	35					
		40							
	2460								
200		800			2.274	6.529	710		
	3260							35.5	1.01
	27.29500								
	2351		10,000	25					
		33+							
	2384+								
200		710			2.204	6.305	664		
	3095							31.	1.23

REVERSIBLE MOLAL HEAT OF DILUTION, L_D, 1.75 cal/mol.

Table XV - Heat of Dilution of 1.55 wt.N. $SrCl_2$.

Time	Res.	$\Delta R \times 10^5$	Gm. Sol.	Mols H_2O	Amp.	E.M.F.	Cal.	Total Ht. Effect.	Heat Effect per Mol.
	27.28500								
	2829		10,000	40					
		25							
	2854								
100		345			2.189	6.238	326.3		
	3199							23.64	0.59
	27.31500								
	2451		10,000	30					
		22							
	2473								
300		1130			2.315	6.619	1099.		
	3603							21.4	0.71
	27.29500								
	2570		10,000	30					
		20							
	2590								
100		310			2.181	6.221	324.2		
	2900							20.92	0.7
	27.30500								
	1988		10,000	20					
		17							
	2005								
100		360			2.316	6.61	365.9		
	2365							17.3	0.86

REVERSIBLE MOLAL HEAT OF DILUTION, L_D, 1.11 cal/mol.

Table XVI - Heat of Dilution of 1.2 wt.N. $SrCl_2$.

Time	Res.	$\Delta R \times 10^5$	Gm. Sol.	Mols H_2O	Amp.	E.M.F.	Cal.	Total Ht. Effect.	Heat Effect per Mol.
	27.26500								
	3634		10,000	35					
		21							
	3655								
200		690			2.13	6.09	620		
	4345							18.9	0.54
	27.24500								
	2055		10,000	25					
		17							
	2072								
200		645			2.12	6.09	618		
	2717							16.3	0.65

REVERSIBLE MOLAL HEAT OF DILUTION? L_D, 0.9 cal/mol

Table XVII - Heat of Dilution of 0.8 wt.N. $SrCl_2$.

Time	Res.	$\Delta R \times 10^5$	Gm. Sol.	Mols H_2O	Amp.	E.M.F.	Cal.	Total Ht. Effect.	Heat Effect per Mol.
	27.35500								
	2494		10,000	40					
		16							
	2510								
100		234			1 .816	5.183	225		
	2744							15.4	0.38
	27.33500								
	2386		10,000	30					
		13							
	2399								
100		226			1.821	5.179	225.5		
	2625							13.	0.44
	27.32500								
	2158		10,000	20					
		11							
	2169								
100		251			1.824	5.201	227.		
	2320							10.	0.50

REVERSIBLE MOLAL HEAT OF DILUTION, L_D, 0.62 cal/mol.

Table XVIII - Heat of Dilution of 0.425 wt.N. $SrCl_2$.

Time	Res.	$\Delta R \times 10^5$	Gm. Sol.	Mols H_2O	Amp.	E.M.F.	Cal.	Total Ht. Effect.	Heat Effect per Mol.
	27.41500								
	2658		10,000	40					
		12							
	2670								
200		490			1.829	5.215	456		
	3160							11.16	0.28
	27.41500								
	1929		10,000	30					
		10							
	1939								
200		451			1.824	5.197	453.1		
	2390							10.07	0.34
	27.41500								
	1920		10,000	20					
		7							
	1927								
200		430			1.827	5.215	455.4		
	2357							7.4	0.37

REVERSIBLE MOLAL HEAT OF DILUTION, L_D, 0.5 cal/mol.

Table XIX - Heat of Dilution of 0.2 wt.N. $SrCl_2$.

Time	Res.	$\Delta R \times 10^5$	Gm. Sol.	Mols H_2O	Amp.	E.M.F.	Cal.	Total Ht. Effect.	Heat Effect per Mol.
	27.47500								
	3344		10,000	40					
		7							
	3351								
200		390			1.796	5.124	440		
	3741							7.88	0.20
	27.47500								
	2603		10,000	30					
		7							
	2610								
200		450			1.791	5.112	437.7		
	3060							6.81	0.23
	27.47500								
	3034		10,000	20					
		4							
	3038								
								4.+	0.2+

REVERSIBLE MOLAL HEAT OF DILUTION, L_D, about 0.25 cal/mol.

Table XX - Heat of Dilution of 3.2 wt.N. NaCl:KCl.

Time	Res.	$\Delta R \times 10^5$	Gm. Sol.	Mols H_2O	Amp.	E.M.F.	Cal.	Total Ht. Effect.	Heat Effect per Mol.
	27.28500								
	3930		10,000	40					
180		180			2.254	6.462	627		
	3750								
300		1207			2.234	6.417	1028		
	4957							-780.	-19.5
	27.26500								
	3685		10,000	30					
300		473			2.288	6.565	1077		
	4158								
300		1202			2.276	6.529	1066		
	5360							-658.	-21.9
	27.28500								
	2134	674	10,000	20					
300					2.29	6.574	1079		
	2808								
300		1190			2.292	6.574	1080		
	3998							-468.	-23.4
	27.28500								
	2293		10,000	10					
300		877			2.292	6.574	1084		
	3170								
300		1142			2.29	6.567	1078		
	4312							-256.	-25.6

OBSERVED REVERSIBLE MOLAL HEAT OF DILUTION, L_D, -27.8 cal/mol.
CALCULATED " " " " " -20.6 cal/mol.

Table XXI - Heat of Dilution of 1.6 wt.N. NaCl:KCl.

Time	Res.	$\Delta R \times 10^5$	Gm. Sol.	Mols H_2O	Amp.	E.M.F.	Cal.	Total Ht. Effect.	Heat Effect per Mol.
	27.28500								
	2169		10,000	40					
200		1331			3.32	9.436	1498		
	3500								
200		1645			3.318	9.436	1497		
	5145							-286.6	-7.16
	27.28500								
	1428		10,000	30					
200		1522			3.49	9.973	1664		
	2950								
200		1760			3.481	9.959	1657		
	4710							-230.7	-7.70
	27.28500								
	2672		10,000	20					
		-170							
	2502								
300		1110			2.295	6.552	1078		
	3612							-165.1	-8.30
	27.26500								
	2880		10,000	10					
		-89							
	2791								
300		1064			2.276	6.489	1059		
	3845							-88.6	-8.86

OBSERVED REVERSIBLE MOLAL HEAT OF DILUTION, L_D, -9.4 cal/mol.

CALCULATED " " " " " -7.13 cal/mol.

Table XXII - Heat of Dilution of 0.8 wt.N. NaCl:KCl.

Time	Res.	$\Delta R \times 10^5$	Gm. Sol.	Mols H_2O	Amp.	E.M.F.	Cal.	Total Ht. Effect.	Heat Effect per Mol.
	27.29500								
	3045		10,000	40					
		-65							
	2980								
300		1200			2.298	6.56	1081		
	4140							-58.54	-1.46
	27.29500								
	2697		10,000	30					
		-55							
	2642								
300		1143			2.311	6.598	1093		
	3785							-52.6	-1.75
	27.28500								
	2690		10,000	20					
		-40							
	2650								
200		750			2.321	6.634	736		
	3400							-39.25	-1.96
	27.29500								
	2813		10,000	10					
		-24							
	2789								
200		743			2.325	6.63	737		
	3532							-23.8	-2.39

REVERSIBLE MOLAL HEAT OF DILUTION, L_D, (OBSERVED) -2.6 cal/mol.

" " " " " (CALCULATED) -2.55 cal/mol.

Table XXIII - Heat of Dilution of 0.4 wt.N. NaCl:KCl.

Time	Res.	$\Delta R \times 10^5$	Gm. Sol.	Mols H_2O	Amp.	E.M.F.	Cal.	Total Ht. Effect.	Heat Effect per Mol.
	27.30500								
	2385		10,000	35					
		-18							
	2367								
100		315			2.32	6.63	368		
	2682							-21.	-0.60
	27.31500								
	2076		10,000	25					
		-16							
	2060								
100		365			2.315	6.60	365		
	2425							-16.	-0.65
	27.30500								
	3010		10,000	15					
		-10							
	3000								
100		355			2.33	6.65	370		
	3355							-10.4	-0.70

REVERSIBLE MOLAL HEAT OF DILUTION, L_D, (OBSERVED) -0.77 cal/mol.

" " " " " (CALCULATED) -1.10 cal/mol.

Table XXIV - Heat of Dilution of 0.2 wt.N. NaCl:KCl.

Time	Res.	$\Delta R \times 10^5$	Gm. Sol.	Mols H_2O	Amp.	E.M.F.	Cal.	Total Ht. Effect.	Heat Effect per Mol.
	27.34500								
	2612		10,000	40					
		-8							
	2604								
100		400			2.30	6.55	361		
	3004							-7.2	-0.18
	27.34500								
	2141		10,000	30					
		-6							
	2135								
100		370			2.29	6.54	358		
	2505							-5.8	-0.19

Another run gave a non-measureable result, probably due to the fact that equilibrium between the solution and the dilution water had not been reached.

REVERSIBLE MOLAL HEAT OF DILUTION, L_D, (OBSERVED) about -0.2 cal/mol.

" " " " " (CALCULATED) -0.55 cal/mol.

Table XXV - Heat of Dilution of 3.2 wt.N. $NaCl:1/2SrCl_2$.

Time	Res.	$\Delta R \times 10^5$	Gm. Sol.	Mols H_2O	Amp.	E.M.F.	Cal.	Total Ht. Effect.	Heat Effect per Mol.
	27.39500								
	2591		10,000	40					
		-340							
	2251								
200		810			2.30	6.56	721.5		
	3061							-303	-7.58
	27.37500								
	2075		10,000	30					
		-265							
	1810								
200		755			2.269	6.48	703.		
	2565							-246.6	-8.22
	27.35500								
	2285		10,000	20					
		-181							
	2104								
200		730			2.29	6.516	713		
	2834							-177.	-8.85
	27.35500								
	1865		10,000	10					
		-95							
	1770								
200		715			2.29	6.534	715		
								-95.	-9.50

REVERSIBLE MOLAL HEAT OF DILUTION, L_D, (OBSERVED) -10.2 cal/mol.

" " " " " (CALCULATED) -8.7 cal/mol.

Table XXVI - Heat of Dilution of 1.6 wt.N. NaCl:1/2$SrCl_2$.

Time	Res.	$\Delta R \times 10^5$	Gm. Sol.	Mols H_2O	Amp.	E.M.F.	Cal.	Total Ht. Effect.	Heat Effect per Mol.
	27.29500								
	4498		10,000	40					
		-120							
	4378								
200		800			2.31	6.57	725.5		
	5178							-108.8	-2.72
	27.29500								
	2257		10,000	30					
		-95							
	2162								
200		729			2.296	6.565	720.5		
	2891							-93.8	-3.13
	27.24500								
	2215		10,000	20					
		-73							
	2142								
200		740			2.28	6.525	711		
	2882							-70.2	-3.51
	27.22500								
	4404		10,000	10					
		-36							
	4368								
200		700			2.28	6.53	712.		
	5068							-36.6	-3.66

REVERSIBLE MOLAL HEAT OF DILUTION, L_D, (OBSERVED) -4.2 cal/mol.

" " " " " (CALCULATED) -3.3 cal/mol.

Table XXVII - Heat of Dilution of 0.8 wt.N. $NaCl:1/2SrCl_2$.

Time	Res.	$\Delta R \times 10^5$	Gm. Sol.	Mols H_2O	Amp.	E.M.F.	Cal.	Total Ht. Effect.	Heat Effect per Mol.
	27.35500								
	2335		10,000	40					
		-30							
	2305								
200		760			2.29	6.53	715		
	3065							-28.2	-0.7
	27.32500								
	1273		10,000	30					
		-26							
	1247								
200		725			2.285	6.55	716		
	1972							-25.7	-0.86
	27.31500								
	1690		10,000	15					
		-16							
	1674								
200		705			2.28	6.50	710		
								-16.1	-1.07

REVERSIBLE MOLAL HEAT OF DILUTION, L_D, (OBSERVED) -1.3 cal/mol.

" " " " " (CALCULATED) -1.18 cal/mol.

Table XXVIII - Heat of Dilution of 0.4 wt.N. NaCl:1/2SrCl$_2$.

Time	Res.	$\Delta R \times 10^5$	Gm. Sol.	Mols H_2O	Amp.	E.M.F.	Cal.	Total Ht. Effect.	Heat Effect per Mol.
	27.30500								
	3967		10,000	40					
		-9							
	3958								
200		740			2.28	6.51	710.		
	4698							-8.65	-0.22
	27.31500								
	0608	-6	10,000	20					
	0602								
100		350			2.28	6.505	354.		
	0952							-6.	-0.30

REVERSIBLE MOLAL HEAT OF DILUTION, L_D, (OBSERVED) about -0.4 cal/mol.

" " " " " (CALCULATED) -0.6 cal/mol.

Table XXIX - Heat of Dilution of 0.2 wt.N. NaCl:1/2$SrCl_2$.

Time	Res.	$\Delta R \times 10^5$	Gm. Sol.	Mols H_2O	Amp.	E.M.F.	Cal.	Total Ht. Effect.	Heat Effect per Mol.
	27.30500								
	0453		10,000	40					
		-5							
	0448								
								(Approx.) -5.	-0.12
	27.28500								
	1609		10,000	25					
		-3							
	1606								
								(Approx.) -3	-0.12

REVERSIBLE MOLAL HEAT OF DILUTION, L_D, (OBSERVED) between -0.1 and -0.2 cal/mol.

Table XXX - Heat of Dilution of 3.2 wt.N. KCl:1/2$SrCl_2$.

Time	Res.	$\Delta R \times 10^5$	Gm. Soln.	MolsH_2O	Amp.	E.M.F.	Cal.	Total Ht. Effect.	Heat Effect per Mol.
	27.26500								
	1569		10,000	40					
300		29			1.71	4.897	600.		
	1598								
300		695			1.709	4.905	601.		
	2292							-575.	-14.37
	27.20500								
	2389		10,000	30					
300		146			1.722	4.915	607		
	2535								
300		655			1.722	4.91	606		
	3190							-472	-15.7
	27.16500								
	2436		10,000	20					
300		399			1.75	4.9505	621		
	2835								
300		660			1.73	4.948	614		
	3495							-343.5	-17.2
	27.14500								
	2573		10,000	10					
300		421			1.705	4.883	597		
	2994								
300		615			1.703	4.883	596		
	3609							-189.	-18.9

REVERSIBLE MOLAL HEAT OF DILUTION, L_D, (OBSERVED) -20.5 cal/mol.

" " " " " (CALCULATED) -9.7 cal/mol.

Table XXXI - Heat of Dilution of 3.2 wt.N. KCl:1/2SrCl$_2$ (Duplicate).

Time	Res.	$\Delta R \times 10^5$	Gm. Sol.	Mols H$_2$O	Amp.	E.M.F.	Cal.	Total Ht. Effect.	Heat Effect per Mol.
	27.22500								
	1494		10,000	35					
300		663			2.305	6.583	1088		
	2157								
300		1258			2.305	6.574	1087		
	3415							-514.8	-14.72
	27.19500								
	1343		10,000	25					
300		745			2.31	6.610	1095		
	2088								
300		1190			2.30	6.603	1090		
	3278							-412.	-16.48
	27.16500								
	1702		10,000	15					
300		863			2.315	6.621	1099		
	2565								
300		1140			2.315	6.603	1096		
	3705							-269.3	-17.95

REVERSIBLE MOLAL HEAT OF DILUTION, L_D, (OBSERVED) -20.7 cal/mol.

Table XXXII - Heat of Dilution of 1.6 wt.N. KCl:1/2SrCl$_2$.

Time	Res.	$\Delta R \times 10^5$	Gm. Sol.	Mols H$_2$O	Amp.	E.M.F.	Cal.	Total Ht. Effect.	Heat Effect per Mol.
	27.28500								
	3227		10,000	40					
		-187							
	3040								
300		380			1.293	3.694	342.5		
	3420								
	27.25500							-168.5	-4.21
	2058		10,000	30					
		-150							
	1908								
200		1410			3.123	8.926	1333		
	3318								
	27.24500							-142.	-4.75
	2796		10,000	20					
		-106							
	2690								
100		690			3.118	8.913	664.3		
	3380								
	27.22500							-102.	-5.10
	3505		10,000	10					
		-55							
	3450								
100		400			2.422	6.824	395.		
	3850							-54.3	-5.43

REVERSIBLE MOLAL HEAT OF DILUTION, L_D, (OBSERVED) -6.0 cal/mol.

" " " " " (CALCULATED) -2.6 cal/mol.

Table XXXIII - Heat of Dilution of 1.6 wt.N. $KCl:1/2SrCl_2$ (Duplicate).

Time	Res.	$\Delta R \times 10^5$	Gm. Sol.	Mols H_2O	Amp.	E.M.F.	Cal.	Total Ht. Effect.	Heat Effect per Mol.
	27.22500								
	2700		10,000	35					
		-165							
	2535								
200		790			2.299	6.556	720.5		
	3325							-150.5	-4.3
	27.19500								
	2548		10,000	25					
		-125							
	2423								
200		720			2.263	6.457	698.6		
	3143							-121.3	-4.86
	27.17500								
	2283		10,000	15					
		-78							
	2205								
200		705			2.26	6.444	696.2		
	2910							-77.	-5.15

REVERSIBLE MOLAL HEAT OF DILUTION, L_D, (OBSERVED) -6.0 cal/mol.

Table XXXIV - Heat of Dilution of 0.8 wt.N. KCl:1/2 $SrCl_2$.

Time	Res.	$\Delta R \times 10^5$	Gm. Sol.	Mols H_2O	Amp.	E.M.F.	Cal.	Total Ht. Effect.	Heat Effect per Mol.
	27.24500								
	3505		10,000	40					
		-35							
	3470								
100		388			2.30	6.56	360		
	3858							-32.4	-0.81
	27.22500								
	3361		10,000	30					
		-29							
	3332								
100		370			2.285	6.525	356		
	3702							-27.9	-0.93
	27.21500								
	3131		10,000	20					
		-21							
	3110								
100		380			2.315	6.60	365		
	3490							-20.2	-1.01

REVERSIBLE MOLAL HEAT OF DILUTION, L_D, (OBSERVED) -1.22 cal/mol.

" " " " " (CALCULATED) -0.53 cal/mol.

Table XXXV - Heat of Dilution of 0.4 wt.N. $KCl:1/2SrCl_2$.

On four dilutions there was no certain effect measured.

L_d, (Observed) is practically 0.00 cal/mol.
" (Calculated) is practically 0.00 cal/mol.

Table XXXVI - Heat of Dilution of 0.2 wt.N. $KCl:1/2SrCl_2$.

Since the 0.4 normal solution gave a value which was too small to be measured, no dilutions were made on this solution. The observed value may be safely assumed to be zero, and the calculated value is zero.

Table XXXVII - Heat of Dilution of 3.2 wt.N. $KCl:SrCl_2$.

Time	Res.	$\Delta R \times 10^5$	Gm. Sol.	Mols H_2O	Amp.	E.M.F.	Cal.	Total Ht. Effect.	Heat Effect per Mol.
	27.27500								
	1935		10,000	35					
		-415							
	1520								
300		1200			2.298	6.549	1079		
	2720							-373	-10.66
	27.22500								
	2492		10,000	25					
		-316							
	2176								
300		1140			2.29	6.529	1072		
	3316							-297.1	-11.88
	27.19500								
	2210		10,000	15					
		-190							
	2020								
300		1120			2.305	6.583	1088		
	3140							-184.6	-12.3

REVERSIBLE MOLAL HEAT OF DILUTION, L_D, (OBSERVED) -14.0 cal/mol.

" " " " " (CALCULATED) -3.9 cal/mol.

Table XXXVIII - Heat of Dilution of 1.6 wt.N. KCl:$SrCl_2$.

Time	Res.	$\Delta R \times 10^5$	Gm. Sol.	Mols H_2O	Amp.	E.M.F.	Cal.	Total Ht. Effect.	Heat Effect per Mol.
	27.24500								
	2219		10,000	35					
		-110							
	2109								
200		818			2.284	6.542	714.5		
	2927							-96.06	-2.75
	27.21500								
	2904		10,000	25					
		-94							
	2810								
200		765			2.272	6.48	703.7		
	3575							-86.47	-3.46
	27.19500								
	2848		10,000	15					
		-64							
	2784								
200		765			2.31	6.583	727.		
	3549							-60.8	-4.05

REVERSIBLE MOLAL HEAT OF DILUTION, L_D, (OBSERVED) -5.2 cal/mol.

" " " " " (CALCULATED) -0.6 cal/mol.

Table XXXIX - Heat of Dilution of 0.8 wt.N. KCl:$SrCl_2$.

Time	Res.	$\Delta R \times 10^5$	Gm. Sol.	Mols H_2O	Amp.	E.M.F.	Cal.	Total Ht. Effect.	Heat Effect per Mol.
	27.23500								
	2995		10,000	35					
		-20							
	2975								
100		385			2.285	6.55	358		
	3360							-18.6	-0.53
	27.23500								
	1367		10,000	25					
		-17							
	1350								
100		375			2.295	6.56	360		
	1725							-16.5	-0.66
	27.21500								
	1970		10,000	15					
		-16							
	1954								
100		360			2.27	6.49	352		
	2314							-15.6	-1.04

REVERSIBLE MOLAL HEAT OF DILUTION, L_D, (OBSERVED) -1.3 cal/mol.

" " " " " (CALCULATED) 0.0 cal/mol.

DISCUSSION.

Figures 8 to 15 show graphically the change of the reversible molal heat of dilution with the concentration. Figures 8 to 10 show this for the three single salts, while in figure 11 the three curves are plotted to the same scale. Figures 12 to 15 show the change of the heat of dilution of the various salt mixtures with their concentrations. There are two curves in each of these three figures. The one labeled "Obs." gives the curve as it was observed experimentally, while that marked"Calc." is plotted from data calculated on the assumption that the heat of dilution of a mixed salt solution is equal to the sum of the heats of dilution of solutions of the various constituents at concentrations equivalent to their concentrations in the mixed solution.

The concentrations, expressed in terms of weight normality, are plotted as abscissae; while the heats of dilution, in calories per mol, are plotted as ordinates.

It will be at once noted that, without exception, the observed values lie on a curve which, except at low concentrations, is significantly higher than the curve for the calculated values. This holds even in the case of the mixed sodium and potassium salts where one would expect the least deviation from the calculated values; and is in harmony with the conclusion (2) that the ion fraction of one of the metallic constituents increases with increasing total salt concentration, since the two

[illegible]

[illegible]

[illegible]

[illegible]

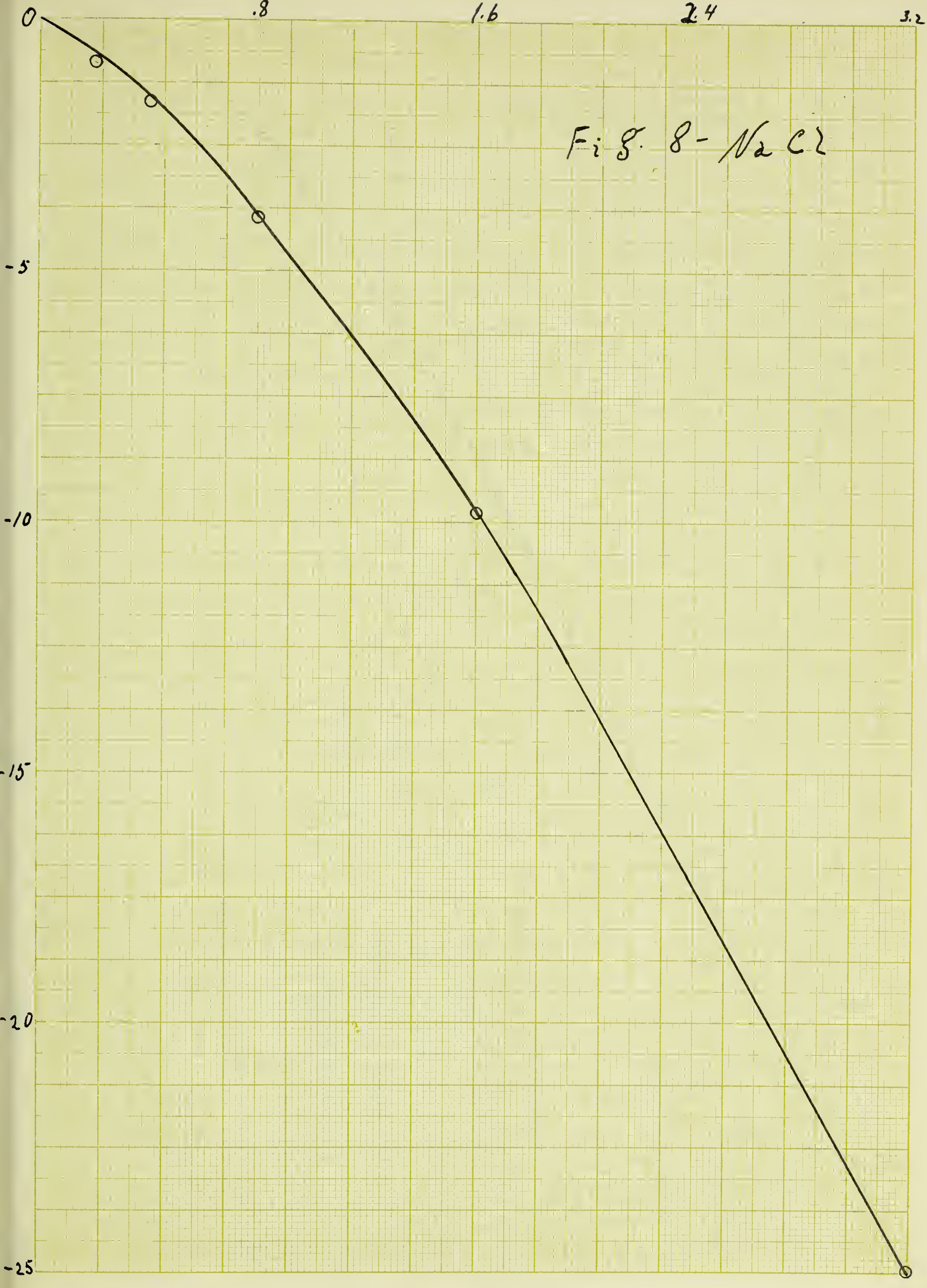


Fig. 8 - NaCl
0
.8
1.6
2.4
3.2
-5
-10
-15
-20
-25

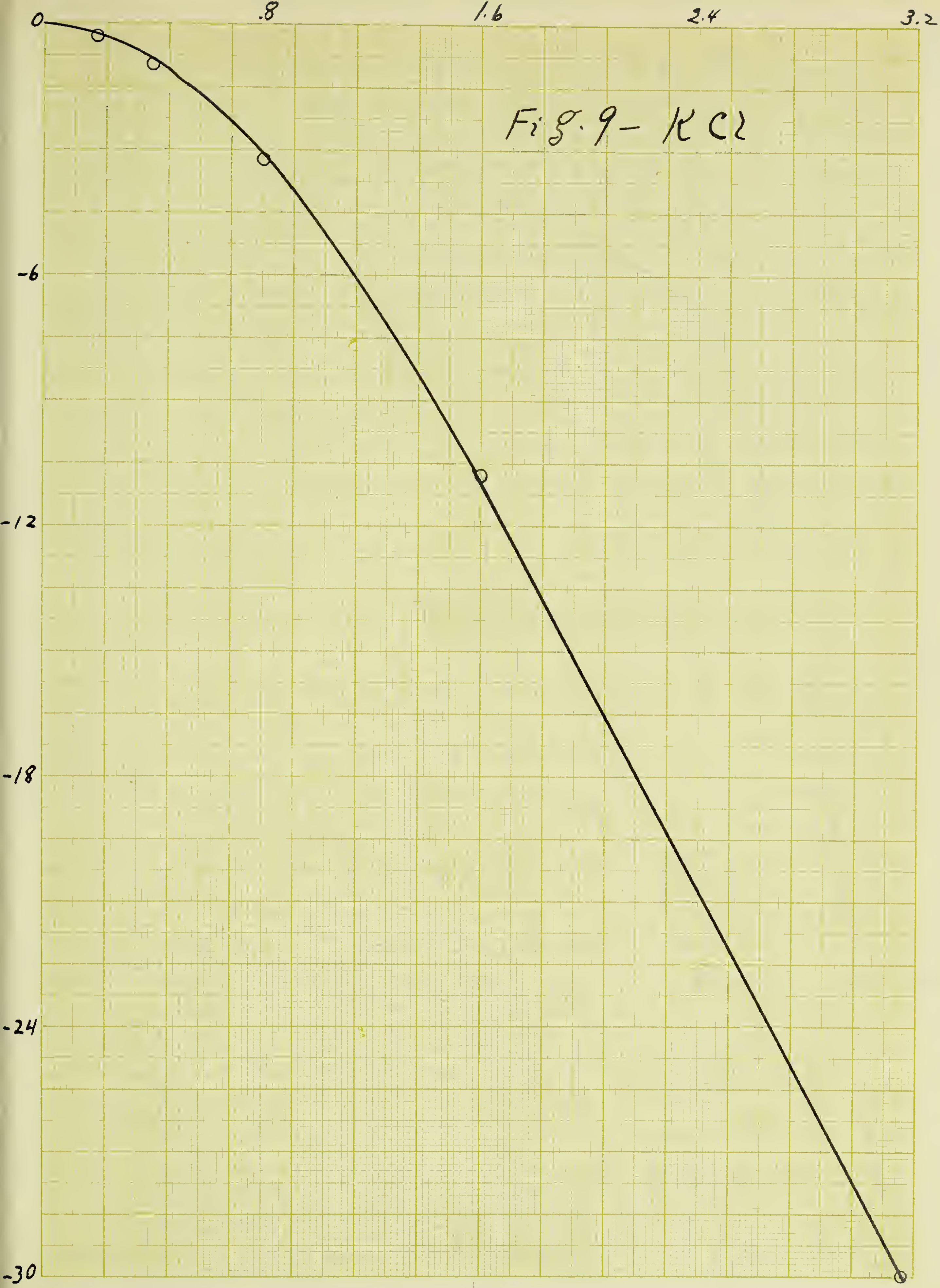


Fig. 9 - KCl
0
.8
1.6
2.4
3.2
-6
-12
-18
-24
-30

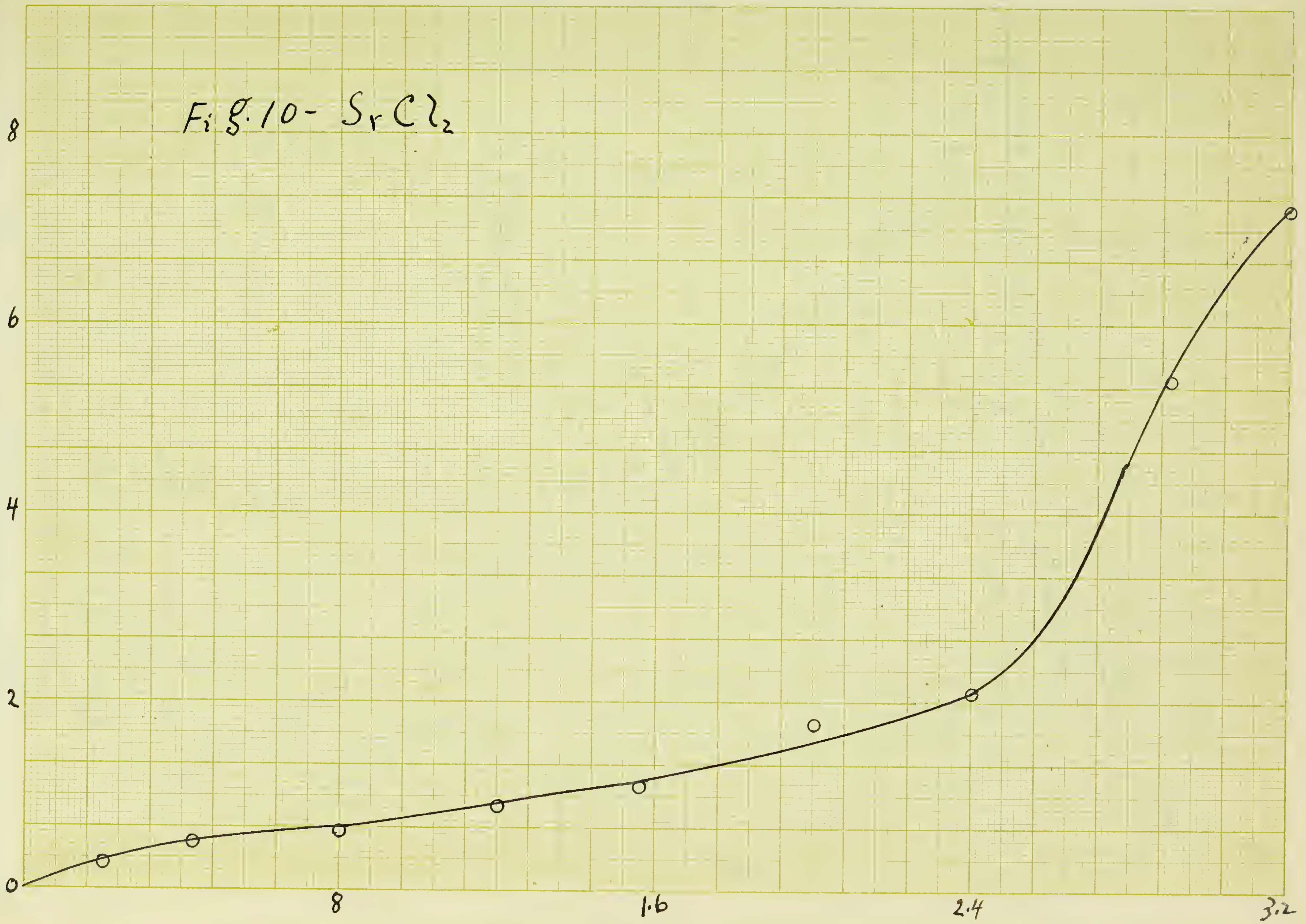


Fig. 10 - $SrCl_2$

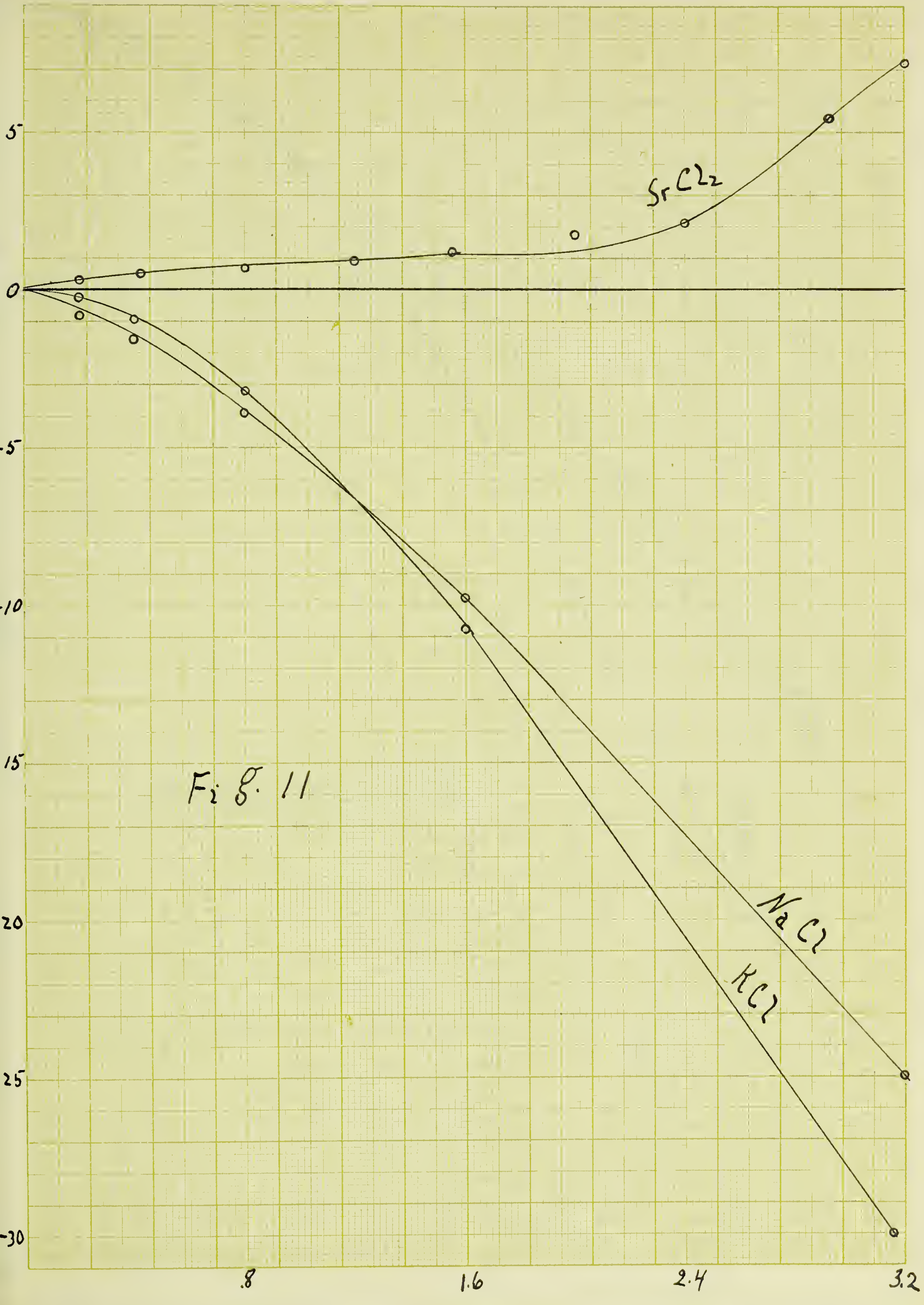


Fig. 11

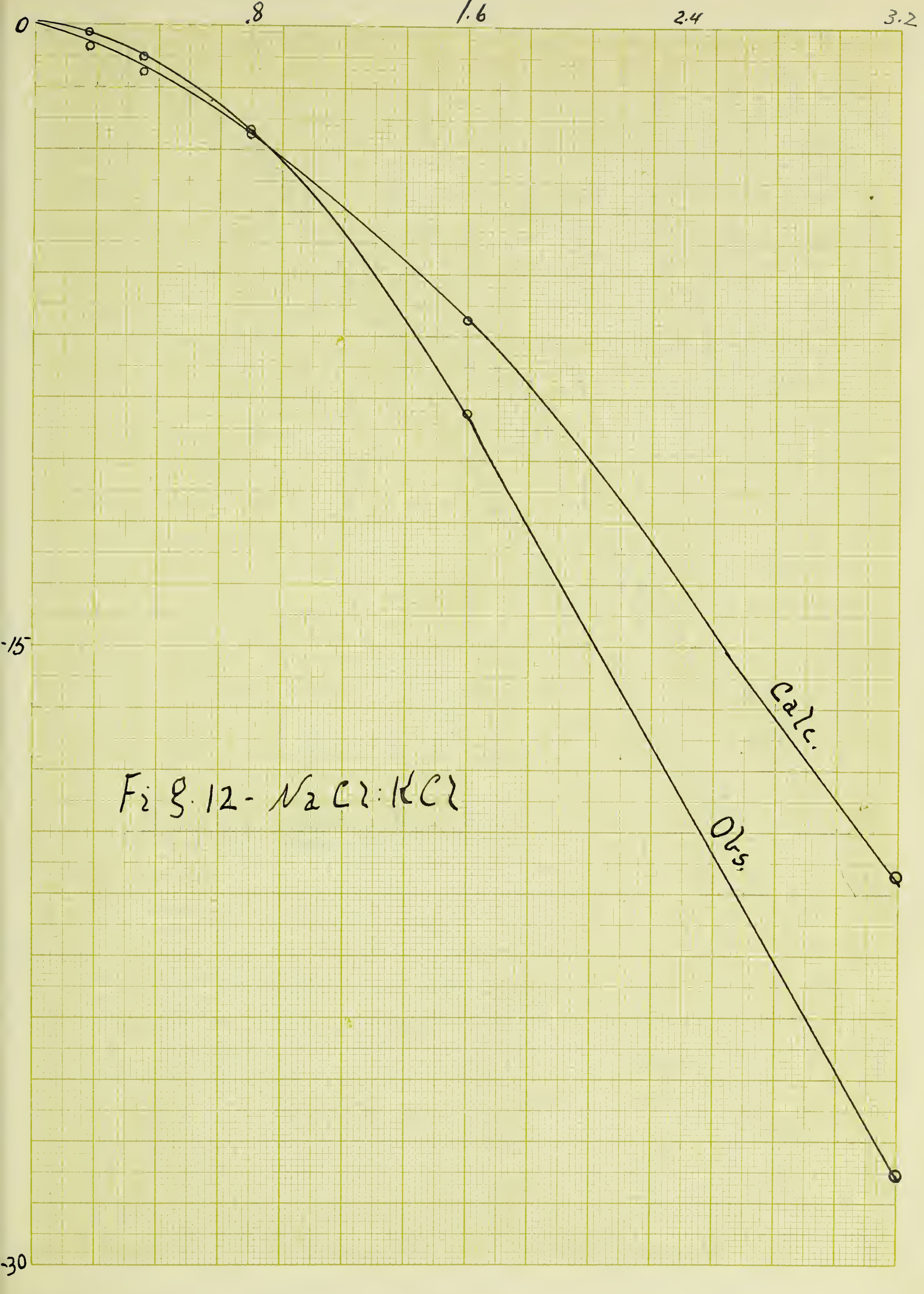


Fig. 12 - NaCl : KCl

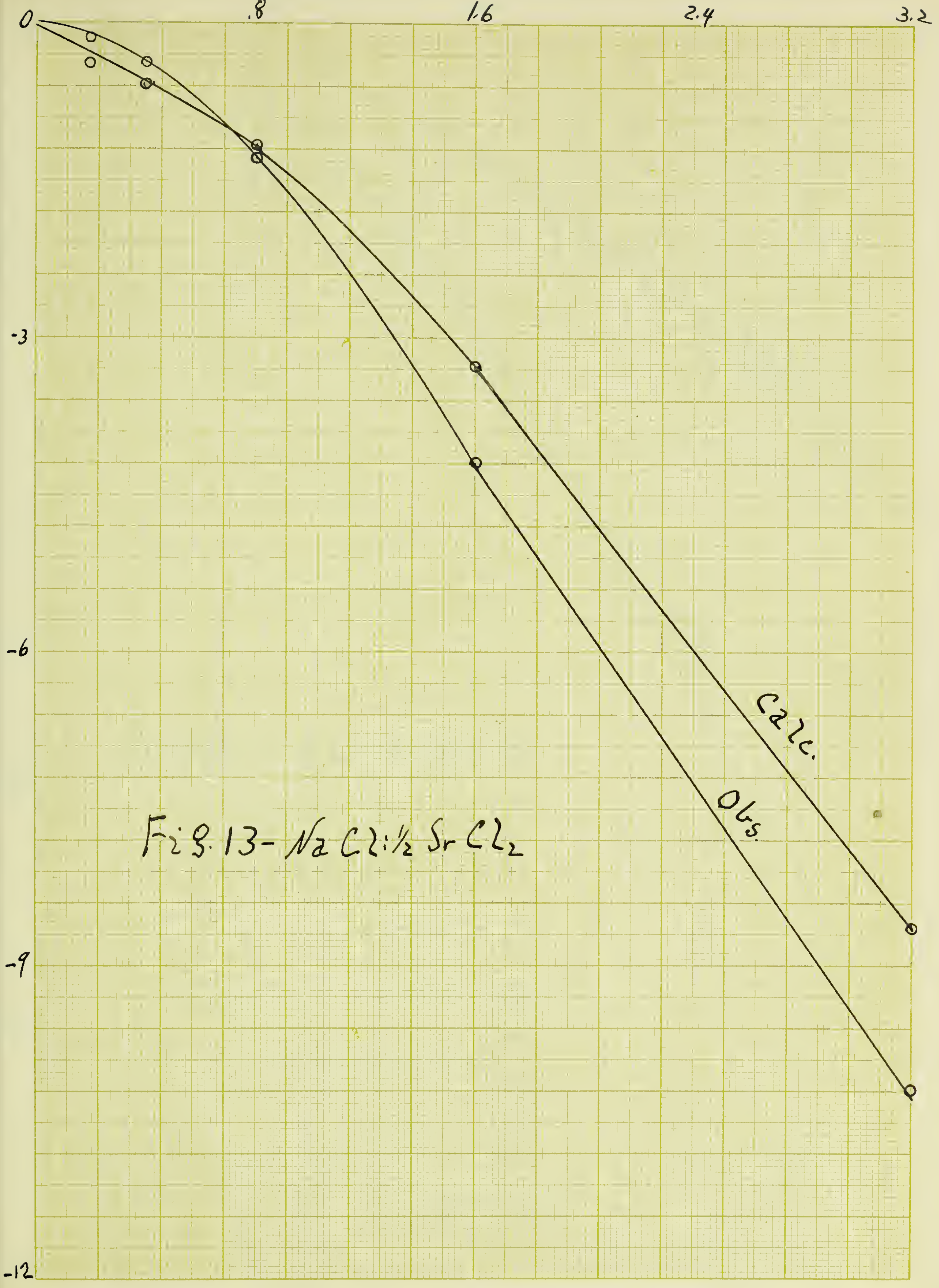


Fig. 13 - $NaCl : \frac{1}{2} SrCl_2$

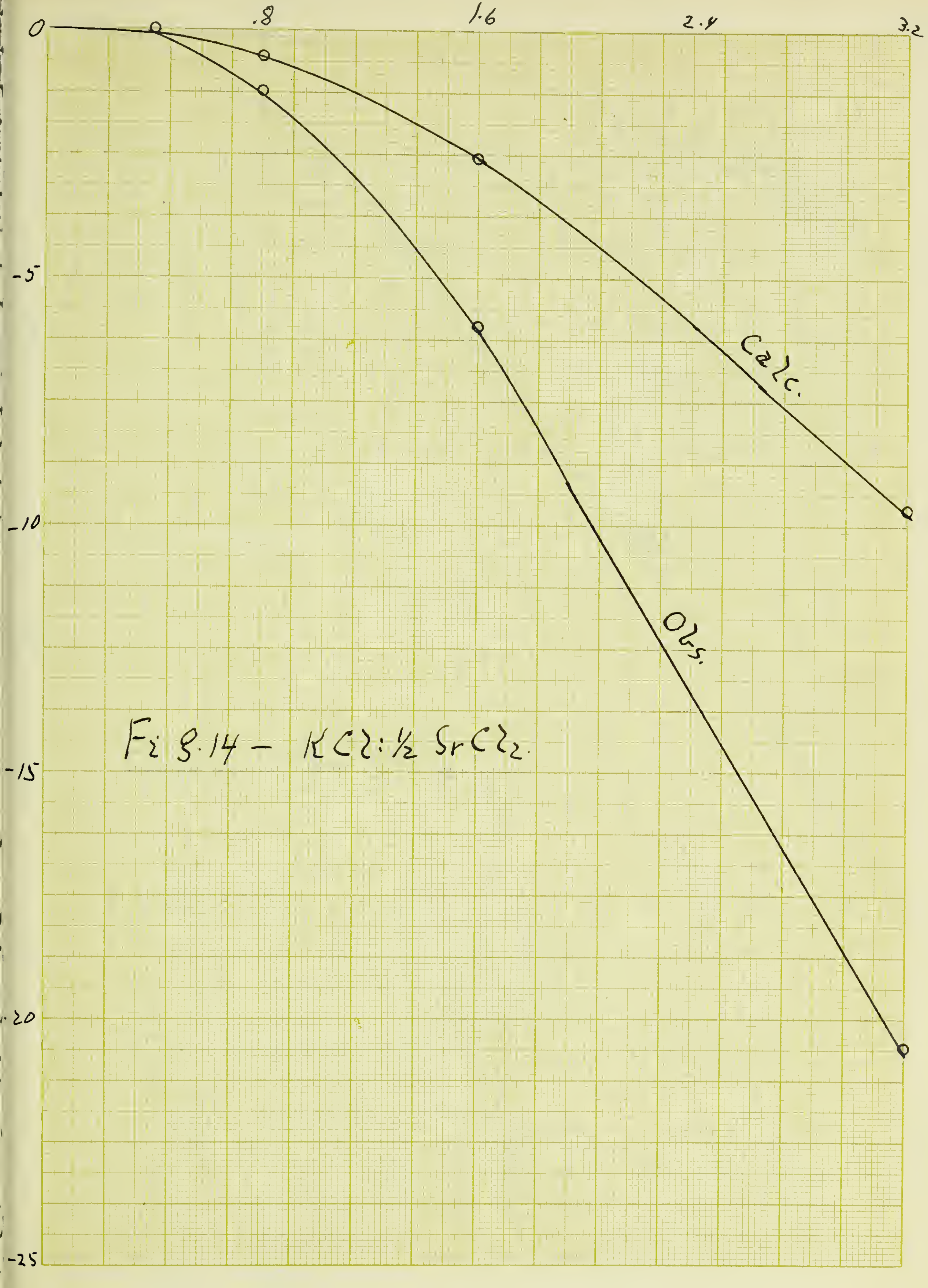


Fig. 14 – $KCl : \frac{1}{2} SrCl_2$.

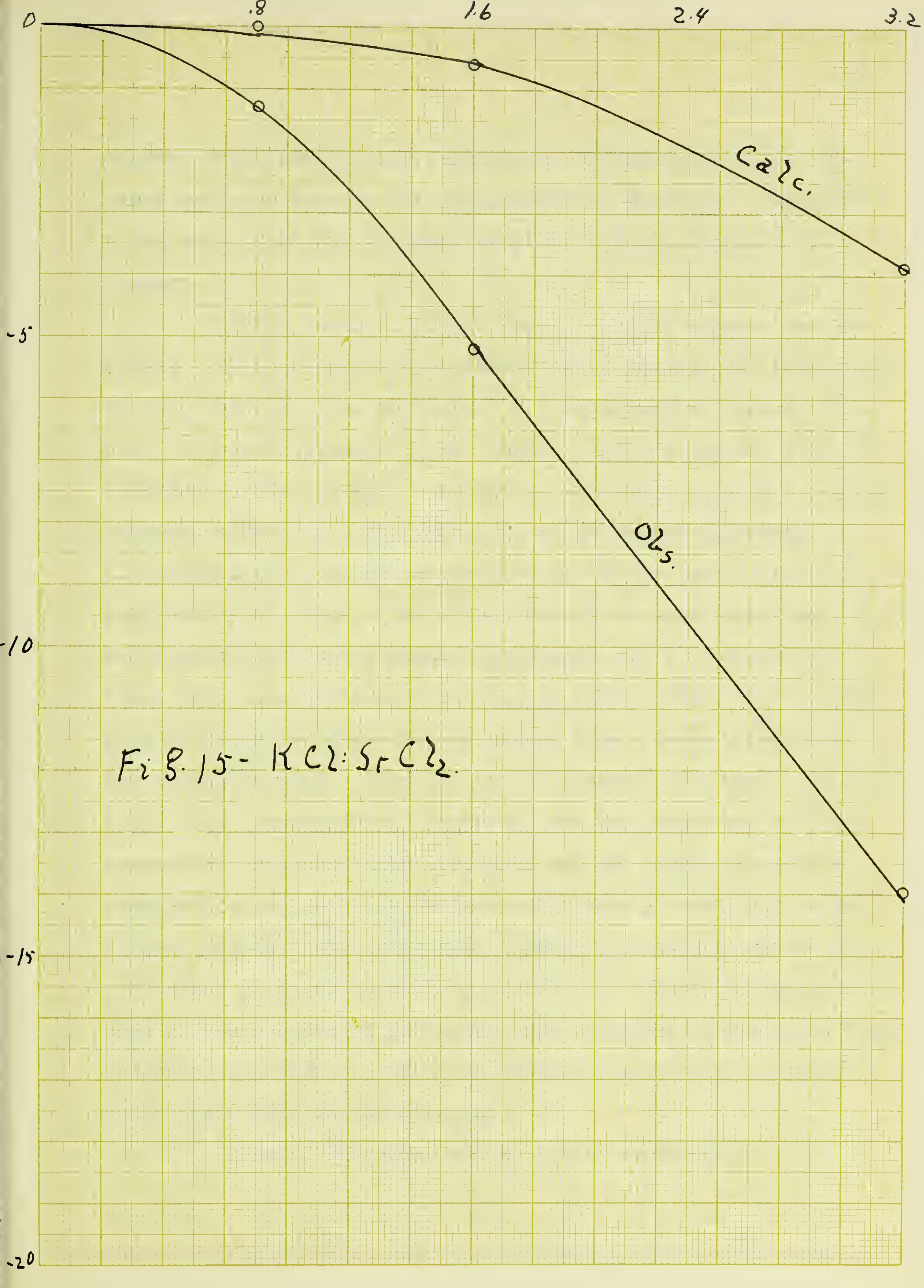


Fig. 15 - KCl: $SrCl_2$.

curves, which practically coincide at low concentrations, diverge more and more as the concentration increases. The curve, to be sure, does not indicate which of the ion fractions increases.

There seems to be no simple relation between the two curves. In the case of the mixture $NaCl:1/2SrCl_2$ the divergence is even less than for NaCl:KCl. The experimental curves, then, seem to be influenced by three factors. There are the specific effects of the two salt components, and there is also the very apparent effect of a third species of molecular aggregate, in all probability a molecular complex of the two salts with varying amounts of water. The concentration of these complexes, in equilibrium with their simple components, will be low at low total salt concentrations, and the specific effect on the curve will be slight so that the two curves should come together at low concentrations. This is, as is observed, the case. As the total salt concentration increases, the concentration of these complexes correspondingly increases and the curve is given a component of slope characteristic of them and depending on two things: namely their individual "heats of dilution" at the concentration at which they occur, which will depend primarily perhaps on their heats of formation; and the rate of change of their concentration with the total salt concentration, or in other words their equilibrium constant.

Thus if the value of **K** in the expression

$$\frac{(KCl_x:NaCl_y)}{(KCl)\ (NaCl)} = K$$

is large, and if the complex $(KCl)_x:(NaCl)_y$ has a high heat of dilution we would expect the slope of the experimental curve to be widely divergent from that of the calculated curve, since a substance of high heat of dilution is being rapidly produced with increasing total salt concentration. If the value of K is small, the curves will diverge less rapidly.

Table XL gives the results of a short series of experiments in which very large quantities of water of dilution were used. The same tendencies will be noticed when such quantities as 5,500 mols of water per 10,000 grams of solution were employed. Table XLI gives a summary of results and it will be noted that in each of the three cases of mixed solutions the observed value of the molal heat effect is greater than the calculated value, a relationship which agrees with those brought out in the curves.

Table XLI.

Salt.	Conc.	Gm. Sol.	Mols H_2O	Observed Ht. Effect	Calc. Ht. Effect
$SrCl_2$	3.2 wt.N.	10,000	5,555	161 cal.	- - -
KCl	3.2 wt.N.	10,000	5,555	-948 "	- - -
NaCl	3.2 wt.N.	10,000	5,555	-1116 "	- - -
NaCl:KCl	3.2 wt.N.	10,000	5,555	-1010 "	-825 cal.
NaCl:1/2$SrCl_2$	3.2 wt.N.	10,000	5,555	-406 "	-390 "
KCl:1/2$SrCl_2$	3.2 wt.N.	10,000	5,555	-542 "	-350 "

Table XL - Heats of Dilution of Various Solutions Using Large Amounts of Water of Dilution.

Time	Res.	$\Delta R \times 10^5$	Gm. Sol.	Mols H_2O	Amp.	E.M.F.	Cal.	Total Ht. Effect.
			I. $SrCl_2$.					
	27.24500							
	2660		10,000	5,555				
		162						
	2822							
200		705			2.26	6.491	701.2	
	3527							161
			II. $SrCl_2$(Duplicate)					
	27.26500							
	2078		10,000	5,555				
		180						
	2258							
300		1170			2.275	6.43	1050	
	3428							161.6
			III. KCl.					
	27.24500							
	2776		10,000	5,555				
		-1037						
	1739							
300		1160			2.277	6.493	1060	
	2899							-948.
			IV. NaCl.					
	27.24500							
	2634		10,000	5,555				
		-1180						
	1454							
300		1120			2.274	6.49	1060	
	2574							-1116.

Table XL (Continued)

Time	Res.	$\Delta R \times 10^5$	Gm. Sol.	Mols H_2O	Amp.	E.M.F.	Cal.	Total Ht. Effect.
			V KCl:NaCl.					
	27.35500							
	2300		10,000	5,555				
		-1100						
	1200							
300		1150			2.263	6.507	1056	
	2350							-1010
			VI. NaCl:1/2$SrCl_2$.					
	27.24500							
	2875		10,000	5,555				
		-415						
	2460							
300		1070			2.263	6.453	1047	
	3530							-406
			VII. KCl:1/2$SrCl_2$					
	27.24500							
	3520		10,000	5,555				
		-580						
	2940							
300					2.282	6.507	1065	
	4080							-542

The formation of these complexes is not out of harmony with experimental data. The substances $2KCl:SrCl_2$ and $2NaCl:SrCl_2$ have both been prepared and isolated (14) and ions of the type $(SrCl_4)^{--}$ and $(BaCl_4)^{--}$ have been referred to as probably existing in solution. (15) Indeed it seems probable that there are very few types of compounds which do not tend to form "higher order compounds". (16)

As was stated in the introduction, the existence of a measureable heat of dilution seems due to the existence of complexes which are formed or decomposed with dilution. (11)

The thermodynamic expression for the reversible molal heat of dilution, L_D, is

$$L_D = RT^2 \frac{d \ln p/p_0}{dT}$$

For a negative value of L_D, as in the case of KCl and NaCl, the equation tells us that the ratio p/p_0 decreases with the temperature. Here p is the vapor pressure of the solution, and p_0 is the vapor pressure of the pure solvent at the same temperature. Thus, if p/p_0 decreases with increasing temperature it means that p increases more slowly with the temperature than p_0, and from Raoult's law this would indicate that at higher temperatures there is an increase in the degree of ionization of the salt. Noyes (17) found experimentally, however, that for salts of this type the opposite was true, namely that the degree of ionization actually decreased with the temperature. There must, therefore, be some factor which aids in determining what

this value shall be, other than simple ionization. The heats of ionization can be obtained from a knowledge of the rate of change of the degree of ionization with the temperature, from the relation

$$\frac{d \ln K}{dT} = \frac{Q}{RT^2}$$

The values calculated from this relationship, however, do not seem to agree with those observed. For instance Arrhenius gives the energy equation for the ionization of dissolved potassium chloride (18) as

$$KCl = K^+ + Cl^- + 362 \text{ cal.}$$

whereas when calculated the value of the heat of ionization is found to be about -2000 calories. According to Senter,"it seems that the process of ionization must be attended by some exothermic reaction which more than compensates for the heat presumably absorbed in splitting up the molecules." Van der Waals (19), as well as Werner, has suggested that ionization in aqueous solution is essentially a hydration process and thus the energy for ionization may come from the combination between the ions and water. The heats of ionization are small in comparison with the heats of hydration. Thomsen (20) has found values as high as 8000 calories per mol of water combining to form a hydrate. Of the two effects this one would therefore be the predominating one. The order of magnitude of the heats of formation of higher order complexes of mixed salts is also great enough to overshadow any ionization effect. A few examples are taken from Pattison Muir's "Elements of Thermal Chemistry", Appendix I.

$SiF_4(aq) + 2KF(aq) = K_2SiF_6(aq) + 23000$ cal.

$NaF + HF = NaHF_2 + 17{,}000$ cal.

$NH_3 + HCl = NH_4Cl + 42{,}000$ cal.

$AuBr_3(aq) + HBr(aq) = HAuBr_4(aq) + 7{,}700$ cal.

These heats are all positive. Now it will be noted in the curves in Figures 13 to 15 that the deviations of the observed values from those calculated are always toward a larger negative heat. That is, with dilution, the complexes formed are broken up with the absorption of heat.

SUMMARY.

1. The reversible molal heat of dilution was determined for solutions of the single salts NaCl, KCl, and $SrCl_2$, at various concentrations ranging from 3.2 wt.N. to 0.2 wt.N., and and also for solutions of the mixed salts NaCl:KCl, NaCl:1/2$SrCl_2$, KCl:1/2$SrCl_2$, and KCl:$SrCl_2$ for the above mentioned range of concentrations.

2. The heats of dilution of KCl and NaCl are negative. This fact in the light of the equation

$$L_D = RT^2 \frac{d \ln p/p_0}{dT}$$

where L_D is the reversible molal heat of dilution, indicates an increase in the degree of ionization with the temperature, contrary to the experimental results of A. A. Noyes, unless explained on the basis of the decomposition of complexes existing in the solution with dilution.

3. The heats of dilution for the solutions of the mixed salts bear no simple additive relation to the heat effects of the single components at equivalent concentrations.

4. The results have been explained on the basis of the conception of higher order compounds as put forth by A. Werner.

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VITA.

The writer of this thesis was born in La Fayette, Indiana. His early education was received, however, in the public schools of Eldon, Missouri, and of St. Louis, Missouri. He entered Leland Stanford Junior University in the autumn of 1912 and graduated with the degree of Bachelor of Arts in Chemistry in the spring of 1915. The following year, 1916, he received the degree of Master of Arts. The thesis consisted of "A Study of the Basic Sulfates of Copper," (Jour. Am. Chem. Soc. 38, 1947 (1916)), and was carried out under the direction of Prof. S. W. Young. During the academic year 1914-1915 he held the position of Teaching Assistant in Chemistry in Stanford University, and during 1915-1916 that of Lecture Preparation Assistant, and Assistant in Toxicology and Medical Organic Chemistry respectively.

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